THE MEASUREMENT AND VALIDITY OF ION-SELECTIVITY ELECTRODE SELECTIVITY COEFFICIENTS UNDER NON-NERNSTIAN CONDITIONS

BY

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A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1986

ACKNOWLEDGEMENTS

I would first like to thank all my relatives and friends who have given me moral support and encouragement not only during the preparation of this work but throughout my formal education.

Thanks should also go to the chairman and members of my supervisory committee for the assistance they have given me in the preparation of this work. Mere words are an inadequate expression of my gratitude to them.

Special thanks go to Dr. Roger G. Bates for providing me with the opportunity to work at The Technical University of Budapest, Hungary, where much of the experimental work reported here was carried out, and for his many helpful suggestions during the writing of this work.

Most special thanks go to Dr. Ernö Pungor, Dr. Klára Toth and all the members of their laboratory group at the Technical University for the help and guidance they gave me during the experimental work, but especially for the warmth and friendship which they so freely bestowed on me.

Köszönöm nagyon szépen!

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Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

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August 1986

Chairman: Herbert A. Laitinen
Major Department: Chemistry

In this work the activity dependence of ion-selective electrode selectivity coefficients measured by conventional methods has been studied, a method for the measurement of selectivity coefficients which are not activity dependent has been developed, and selectivity coefficients measured by this new method have been evaluated with regard to their ability to describe the behavior of the electrode in mixed solutions containing both primary and interfering ions. Three electrode types were used: a neutral carrier electrode responsive to calcium and barium ions, a neutral

carrier electrode responsive to sodium and calcium ions, and a liquid ion-exchanger electrode responsive to calcium and barium ions.

Initially selectivity coefficients were measured over a wide range of activities by conventional methods, including the separate solution method at equal activities, the mixed-solution graphical cross-point method, and curve-fitting, which are all based on the Nicolsky equation. These coefficients showed a marked activity dependence.

It was noticed that the response slopes for the electrodes differed from the Nernstian values, and the ratio of the response slopes for the primary and interfering ions did not equal the ratio of the ionic charges, as is assumed in the Nicolsky equation. The Nicolsky equation was modified to include the slope ratio rather than the charge ratio, and selectivity coefficients based on this modified Nicolsky equation were measured, using separate solutions. These coefficients showed little or no activity dependence over the range of activities for which electrode response was linear.

The modified Nicolsky equation was then used to predict the potential of the electrodes in mixed solutions. The predicted potentials agreed fairly well with measured potentials, within the reproducibility of the measurements.

It is concluded that the apparent activity dependence

of selectivity coefficients is a result of assuming Nernstian electrode behavior. The recommended method for measuring selectivity coefficients involves measuring electrode potentials in separate solutions of primary and interfering ions over a wide range of activities, and using the modified Nicolsky equation. This produces activity-independent selectivity coefficients which adequately describe the electrode behavior in mixed solutions, while providing a check on linearity and response slope.

CHAPTER 1
INTRODUCTION

The term "ion-selective electrode" refers to a group of electrodes whose principal component, usually a membrane, yields a potential in response to the presence of one (or several) ionic species, in the presence of other ionic species. A wide variety of substances can be used in the membrane, including glasses, charged liquid ion-exchangers, solid crystals, insoluble precipitates, neutral complexing agents, and enzymes. The structure of a typical ion-selective electrode is shown in Figure 1.

Although the current interest in ion-selective electrodes dates from the development in the 1960's of the precipitate-based heterogeneous membrane electrode by Pungor and co-workers (1) and the development of the single-crystal lanthanum fluoride electrode by Frant and Ross (2), the first ion-selective electrode was actually developed much earlier. This was the pH glass electrode introduced by Cremer in 1906 (3), the forerunner of the variety of glass electrodes, for hydrogen and other cations, which are in common use today.

In the early thirties studies of the electrochemical behavior and composition of glass membranes by Lengyel and

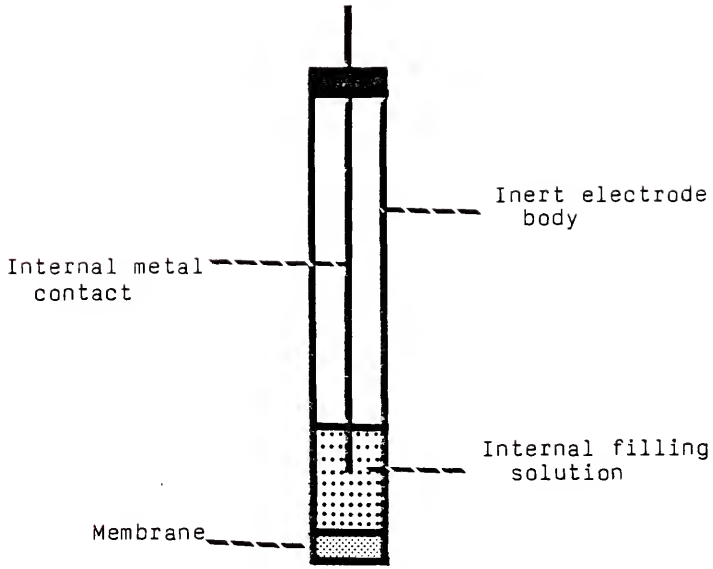

FIGURE 1. Ion-Selective Electrode Structure.

Blum (4) resulted in the development of the alkali-sensitive membranes. The first solid-crystal membrane electrode was introduced by Kolthoff and Sanders (5) in 1937, and consisted of a fused silver halide melt sealed with wax to a glass tube; a 0.01 molar halide solution was used as internal filling solution and a silver/silver halide electrode was inserted as the internal reference. The electrode was sensitive to halide ion and was superior to the conventional Ag/AgCl electrode in that it was insensitive to oxidizing agents, such as permanganate, and produced a sharper break in potentiometric titration curves.

The first liquid-membrane electrodes were prepared by Sollner and Shean in 1964 (6), and consisted of a hydrophobic membrane containing a liquid ion-exchanger. The first neutral carrier liquid-membrane electrodes were developed by Stefanac and Simon (7), who used the antibiotics monactin, nonactin and valinomycin to produce electrodes selective for alkali metal ions. Other neutral carriers, such as cyclic polyethers ("crowns") and polyesters, have also been employed as neutral carriers (8-9).

In 1969 Guilbault and co-workers introduced the enzyme electrode, in which an ion-selective electrode is covered by a polymeric matrix containing the enzyme (10-11). The enzyme (urease, for example) reacts with the analyte (urea) to produce an ion (ammonium ion) which is sensed by the ion-selective electrode. A similar principle is involved in the

gas-sensing electrode (12), in which the gas passes through a gas-permeable membrane and reacts with an internal solution to produce an ion, which is then detected by an ion-selective electrode.

The newest type of ion-selective electrode is the Ion Sensitive Field Effect Transistor (ISFET). The ISFET (13) is a conventional Field Effect Transistor on which a layer of ion-sensitive material, such as silicon dioxide, silicon nitride, or a valinomycin/plasticizer/polyvinyl chloride mixture, has been deposited.

As can be seen from the above, a wide variety of ion-selective electrodes is now available. Several classification schemes have been proposed for these electrodes (14-16), but perhaps the best is a classification, given in Table 1 (17), based on the type of material used in the construction of the electrodes.

TABLE 1
PRESENT CLASSIFICATION OF ION-SELECTIVE ELECTRODES

A. MONOMEMBRANE ELECTRODES

1. Homogeneous, fixed-site, ion-exchange membranes--e.g., ion-exchange cellulose paper and polyquinhydrone-HCOH membranes (for pH measurements).
2. Homogeneous, fixed-site, non-glass solid-state crystal, or pressed pellet membranes--e.g., Ag_2S, AgCl and LaF_3 membranes.
3. Homogeneous, fixed-site, glass membranes--e.g., pH sensitive glass membrane and cation sensitive glass membranes.
4. Homogeneous, mobile-site, liquid ion-exchange membranes--e.g., long-chain ion-exchange materials, such as the alkyl phosphate salts and the tetraalkyl ammonium salts.
5. Homogeneous, site-free, electroneutral macrocyclic ion carriers--e.g., valinomycin, nonactin, monactin and synthetic crown ethers.
6. Immobilized liquid membranes--e.g., liquid ion-exchangers or neutral carriers immobilized in PVC (polyvinyl chloride) matrices.
7. Homogeneous, semiconductor membranes--e.g., Ge, InSb, Si, PbO_2 and MnO_2 membranes.
8. Heterogeneous, fixed-site, solid-state crystal membranes--e.g., electroactive materials such as silver halide crystals imbedded in supporting matrices (silicone rubber or ceramics).

B. MULTIMEMBRANE ELECTRODES

1. Immobilized enzyme electrodes--e.g., urease enzyme electrode (an immobilized enzyme matrix coated on an ion-selective electrode).
2. Gas sensing electrodes--e.g., CO_2 electrode and SO_2 electrode (a hydrophobic membrane such as Teflon placed over an ion-selective electrode (usually a pH electrode) with a solution between the membrane and pH sensing glass).

CHAPTER 2
THE POTENTIAL RESPONSE OF ION-SELECTIVE ELECTRODES

The attractiveness of ion-selective electrodes lies in their ability to produce a potential which is dependent on the activity of a given ion in solution, and which is either independent of or considerably less dependent on the activity of any other ions which may also be present. The source of this potential has been the subject of a number of theories.

The earliest theories, not surprisingly, were developed for the glass electrodes (18-22). Of these theories the ion-exchange theory developed by Eisenman (23), a refinement of the theory introduced by Nicolsky, has gained general acceptance.

In the Eisenman theory it is assumed that the principal potential-determining reaction is the exchange of ions in the glass with ions in the external solution:

$$I^+ \text{ (glass)} + J^+\text{(aqueous)} \rightleftarrows J^+\text{(glass)} + I^+\text{(aqueous)};\ \Delta G^{\circ}_{ij} \qquad (1)$$

where I^+ and J^+ are ionic species and ΔG°_{ij} is the standard free energy change for the reaction. At equilibrium the ionic electrochemical potentials, ($\bar{\mu}_i'$), in the glass must be equal to those ($\bar{\mu}_i$) in the solution, and can be expressed in terms of the chemical potential μ_i and the electrostatic potential ψ:

$$\bar{\mu}_i = \mu_i + z_i F \psi \qquad (2)$$

where z_i is the charge on ion I and F is Faraday's constant. The chemical potential can be expressed in terms of the standard chemical potential, μ_i^o, and the activity, a_i or a_j, of the ion:

$$\mu_i = \mu_i^o + RT \ln(a_i) \qquad (3)$$

where R is the Universal Gas Constant and T is the Kelvin temperature. Adding the assumption that the activity of the ion in the glass is proportional to the nth power of its mole fraction, where n is a whole number, one obtains an expression for the electrode potential, E:

$$E = E^o + \frac{RT}{F} \ln(a_i^{1/n} + K_n^{1/n} a_j^{1/n})^n \qquad (4)$$

where E^o is the standard potential and K_n is a selectivity parameter given by

$$K_n = \frac{a_i}{a_j} \left[(1-X_i') / X_i'\right]^n \qquad (5)$$

where X_i' is the mole fraction of the ion in the glass.

The Eisenman theory developed for glass electrodes is also applicable, with some modifications, to liquid-membrane electrodes based on liquid ion-exchangers (24). In a liquid-membrane electrode based on a liquid ion-exchanger, a membrane containing the ion-exchanger separates two aqueous solutions. One of the solutions is maintained at a constant concentration and is considered to be the internal filling

solution. The other (external) solution is the test solution.

In the case of liquid ion-exchange membranes the exchange sites are not fixed rigidly in place, as they are in glass, but are charged species free to move throughout the membrane. The membrane is assumed to be ideally permselective, permitting only ions opposite in charge to the exchanger to enter the membrane from the aqueous solutions. The neutral species formed by the association of exchange site and counter-ion is assumed to be in equilibrium with the free sites and counter-ions throughout the membrane, and the mobilities of all species within the membrane are assumed to be constant.

Under these conditions it is possible to obtain an expression for E, the electrode potential:

$$E = -\frac{RT}{Fz_i}\ln\frac{\sum_i u_i k_i a_i''}{\sum_i u_i k_i a_i'} - \int_o^d t_o \, d\ln\frac{\sum_i \frac{u_{is}}{K_i}c_i}{\sum_i u_i c_i} - \int_o^d \frac{\frac{u_s J_s^*}{RT}dx}{(u_s+\sum_i \frac{u_{is}}{K_i}c_i)\sum_i u_i c_i + u_s c_s \sum_i \frac{u_{is}}{K_i}c_i} \qquad (6)$$

where the subscript "i" refers to the counter-ion, the subscript "s" refers to the exchange site, and the subscript "is" refers to the associated species. The symbols u, a, z and c represent the mobility, activity, charge and

concentration of the species indicated by subscript. K_i is the equilibrium constant for the dissociation of the complex, J_s^* is the total flux of all site species, d is the thickness of the membrane, and the 'and" refer to the two solutions in contact with the membrane. The symbols R, F and T have their usual meanings. The parameter k_i is essentially a thermodynamic equilibrium constant for the distribution of the ion between the solution and the membrane. The value of k_i is given by

$$k_i = \exp\left(\frac{\mu_i^o - \mu_i^{o(m)}}{RT}\right) \tag{7}$$

where u_i^o is the standard chemical potential of species i, and m refers to the membrane.

The parameter t in Eqn. 6 is merely a collection of mathematical terms inserted for convenience. It is equal to

$$t = \frac{u_s c_s}{\left(\sum_i \frac{u_s c_s}{u_{is} c_{is}} + 1\right) \sum_i u_i c_i + u_s c_s} \tag{8}$$

For the special case of a steady state (J_s^* equal to zero) in which two counter-ions are present and the association of counter-ions and sites is strong, it is possible to solve Eqn. 6 explicitly:

$$E = \frac{RT}{Fz_i}(1 - \tau) \ln \frac{\sum_{i=1}^{2} (u_i + u_s) k_i a_i'}{\sum_{i=1}^{2} (u_i + u_s) k_i a_i''} + \tau \ln \frac{\sum_{i=1}^{2} \frac{u_{is}}{K_i} k_i a_i'}{\sum_{i=1}^{2} \frac{u_{is}}{K_i} k_i a_i''} \tag{9}$$

where τ is given by

$$\tau = \frac{u_s\left(\frac{u_{2s}}{K_2} - \frac{u_{1s}}{K_1}\right)}{(u_1 + u_s)\frac{u_{2s}}{K_2} - (u_2 + u_s)\frac{u_{1s}}{K_1}} \qquad (10)$$

When the internal filling solution (kept at constant concentration) is the one designated with the ', Eqn. 9 can be written as

$$E = RT/Fz_i\left[C + (1 - \tau)\ln\left(1 + \left[\frac{u_1 + u_s}{u_2 + u_s}\frac{k_1}{k_2} - 1\right]X_1''\right)\right. \qquad (11)$$

$$\left. + \tau \ln\left(1 + \left[\frac{u_{1s}}{u_{2s}}\frac{K_2}{K_1}\frac{k_1}{k_2} - 1\right]X_1''\right)\right.$$

Where X_1'' is the mole fraction of species i in the solution on the side of the membrane designated " (the external solution).

Buck and others have treated the response of an ion-exchange membrane electrode using the Teorell-Meyer-Sievers model (25-26). In this approach the electrode potential is taken to be the sum of three potentials: a Donnan potential established at the interface between the test solution and the membrane, a potential resulting from diffusion and migration within the membrane, and a second Donnan potential established at the interface between the membrane and the internal solution.

The diffusion-migration potential ($\phi^{II} - \phi^{I}$) for a negatively charged mobile site membrane is given by

$$\phi^{II} - \phi^{I} = (URT/F)\ln(m_+^{I}/m_+^{II}) \qquad (12)$$

where I and II refer to the boundaries of the membrane, m is

the molal concentration and U is dependent upon the ionic mobilities:

$$U = (u_+ - u_-)/(u_+ + u_-) \qquad (13)$$

The electrode potential E is then

$$E = \frac{RT}{F} \ln \left(\frac{r_+^{II} \bar{\gamma}_-^{I} \gamma_+^{II}}{r_+^{I} \bar{\gamma}_+^{II} \gamma_+^{I}}\right) + \frac{URT}{F} \ln\left(\frac{r_+^{I} \bar{a}_\pm^{I} \bar{\gamma}_+^{II}}{r_+^{II} \bar{a}_\pm^{II} \bar{\gamma}_+^{I}}\right) \qquad (14)$$

where γ is the single ion activity coefficient in the membrane, $\bar{\gamma}$ is the single ion-activity coefficient in the solution, r_+ is the ratio of the molal concentration of the cation in the membrane to that in the solution, and $\bar{a}_\pm$ is the mean molal ion activity in the solution.

This model predicts that as the activity in the external test solution is increased, keeping the activity in the internal solution constant, a region will be reached in which Donnan Exclusion fails and co-ions enter the membrane. The magnitude and sign of the slope of the response are then dependent on the value of U, and are equal to $2U/(1 + U)$. At very high activities, for membranes with large negative values of U this model predicts a third linear region, with a slope equal to URT/F. Using the liquid ion-exchanger Aliquat 336S, Buck and co-workers were able to demonstrate experimentally the validity of this approach (27-32).

For liquid-membrane electrodes containing a neutral ligand (carrier) rather than a charged exchanger, Morf has proposed a model similar to the Eisenman model (33). For

the case in which two cations of equal charge are present, the membrane potential is given by

$$E_m = \frac{RT}{zF} \ln \left\{ \frac{\sum_n u_{is,n} K_{i,n} a_i' + \sum_n u_{js,n} K_{j,n} a_j'}{\sum_n u_{is,n} K_{i,n} a_i'' + \sum_n u_{js,n} K_{j,n} a_j''} \right\} \qquad (15)$$

where n is the number of neutral ligands (s) present in the metal-ligand complex, i and j are the two cations, the ' and " denote the two membrane surfaces, and K is the distribution parameter, given by

$$K_{m,n} = k_m \frac{a_{ms,n}(x)}{a_m(x)} = \beta_{ms,n} k_m a_s \qquad (16)$$

where m refers to the cation, k_m is the distribution coefficient for the cation distributing between the membrane phase and the external solution, $a_{ms,n}(x)$ is the activity of the complex MS_n^{z+} in the membrane, $a_m(x)$ is the activity of the cation in the membrane, $\beta_{ms,n}$ is the stability constant for the complex in the membrane, and a_s is the activity of the ligand S in the membrane phase.

Regardless of whether the electrode membrane is treated as a solid ion-exchanger, a liquid ion-exchanger or a semi-permeable membrane at which Donnan equilibrium is established, the electrode potential is found to be dependent on ion activity in a logarithmic fashion. It has been

generally assumed in practice that the behavior of any ion-selective electrode can be described by the Nernst equation (34):

$$E = E^{o} + \frac{RT}{nF} \ln a_{A} \qquad (17)$$

CHAPTER 3
THE SELECTIVITY OF ION-SELECTIVE ELECTRODES

The oldest, and still the most widely used, parameter for the quantitative description of the selectivity of an ion-selective electrode is the Nicolsky parameter, $k^{pot}_{A,B}$, as it appears in the well-known Nicolsky equation (35):

$$E = \text{constant} + \frac{2.303RT}{z_A F} \log \left(a_A + k^{pot}_{A,B} (a_B)^{z_A/z_B}\right) \qquad (18)$$

where A and B are species to which the electrode responds, z represents the charge on the species and a is the activity.

Based upon this equation a number of methods for the experimental determination of $k^{pot}_{A,B}$ have been developed (36). These can be grouped into two main categories, the separate solution and the mixed solution methods. Separate solution methods use pure solutions of the ion to which the electrode gives the maximum response (the primary ion A) and of another ion (the secondary or interfering ion B) to which the electrode also responds. Mixed solution methods use solutions containing both the primary and the interfering ions.

When separate solutions are used, two approaches may be taken. The potential of the electrode may be measured in pure solutions containing identical activities, usually

0.1 M, of the primary or interfering ion; in this case $k^{pot}_{A,B}$ is given by

$$\log k^{pot}_{A,B} = \frac{E_B - E_A}{2.303RT/F} + \log a_A^{(1-z_A/z_B)} \qquad (19)$$

On the other hand, the activities of the ions may be adjusted so that the two potentials, E_A and E_B are equal. In this case

$$k^{pot}_{A,B} = \frac{a_A}{a_B^{(z_A/z_B)}} \qquad (20)$$

A number of approaches are possible also when using mixed solution data. Light and Swartz (37) have used a comparison of the potential measured in a solution of pure primary ion (E_A) and that measured in a solution containing the same concentration of the primary ion in addition to some amount of the interfering ion (E_{AB}). The selectivity coefficient is then given by

$$\log k^{pot}_{A,B} = \frac{(\frac{E_A - E_{AB}}{RT/F})a_A - a_A}{a_B} \qquad (21)$$

A graphical approach has also been used with mixed solution data, requiring potential measurements in a number of mixed solutions of varying concentrations (36,38). A series of solutions are prepared, all containing one of the ions at a fixed concentration and the other ion at varied concentrations. The potentials measured in these solutions are then plotted as a function of the concentration of the ion which is varied. If one is careful to use ions for

which the selectivity coefficient is roughly 0.01 to 1, a curve similar to that shown in Figure 2 is obtained. At the low concentration end the electrode is assumed to be responding only to the ion whose concentration is fixed, and the potential does not change. At the high concentration end the electrode is presumed to be responding only to the ion whose concentration is being varied. Thus two linear equations can be written:

$$E = E_A^o - \frac{RT}{Z_A F} \ln(a_A) \tag{22}$$

$$E = E_B^o - \frac{RT}{Z_B F} \ln(a_B) = E_A^o - \frac{RT}{Z_A F} \ln (k_{A,B}^{pot} a_B^{Z_A/Z_B}) \tag{23}$$

The activity at which the two linear portions intersect can then be used to calculate $k_{A,B}^{pot}$:

$$k_{A,B}^{pot} = \frac{a_A}{(a_B)^{(Z_A/Z_B)}} \tag{24}$$

Computer curvefitting has also been used with the mixed solution method (39). Potentials are measured in a number of solutions containing various concentrations of both of the ions. The data are then fitted to the Nicolsky equation by varying the parameters $k_{A,B}^{pot}$, RT/zF and the constant (E^o) to achieve the minimum difference between the measured potentials and those calculated from the Nicolsky equation.

In addition to the methods based on the Nicolsky equation, several other methods have been suggested for the measurement of the selectivity coefficient. Buck (40) has suggested that in fact two types of selectivity behavior may

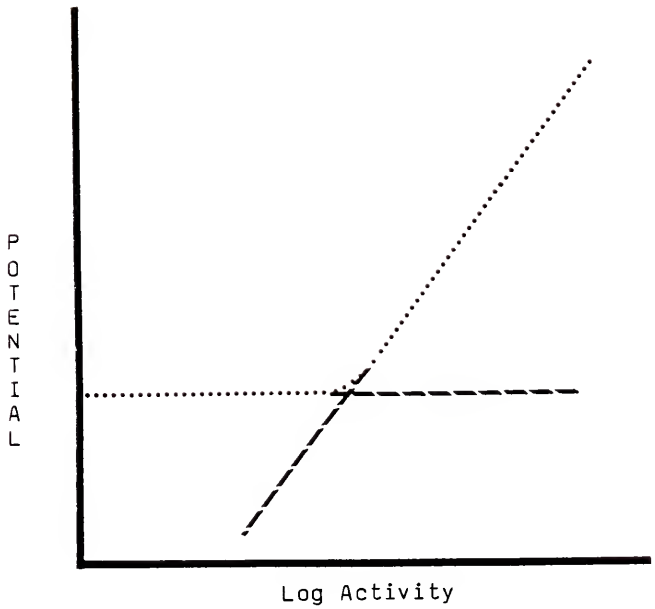

FIGURE 2. The Graphical Cross-point Mixed Solution Method for Measurement of $k^{pot}_{A,B}$.

be exhibited by an electrode, in view of the Teorell-Meyer-Sievers model. If the interfacial processes are rapid and reversible and the integrals in the diffusion potential equation can be exactly solved, then the behavior is in accord with the Nicolsky equation. If the interfacial processes are not at equilibrium, however, or the diffusion potential depends on the path of integration (as would be the case if co-ions are present or if other complexes or ion pairs can form), the apparent selectivity coefficient, k (app), depends not only on the activities of the two ions but also on their relative activities:

$$\ln k^{pot}_{A,B}\ (app) = \ln \{\exp(E_{AB} - E_A)/S-1\} - \ln(\frac{a_B}{a_A}) \qquad (25)$$

where S is the calibration slope for the primary ion A, E_A is the potential measured in a pure solution of A and E_{AB} is that measured in mixed solution. Buck advocates using three or four different concentrations of pure primary ion in addition to about fifteen mixtures of primary and interfering ions. The selectivity coefficient $k^{pot}_{A,B}$ (app) is then calculated according to Eqn. 25, and its logarithm plotted as function of the logarithm of a_B/a_A. If a horizontal line results, then $k^{pot}_{A,B}$ (app) is equal to $k^{pot}_{A,B}$, the Nicolsky selectivity coefficient.

Mohan and Rechnitz (41) and Hakoila and co-workers (42) have presented an empirical equation for the calculation of the selectivity coefficient, KS, for electrodes which do not exhibit Nernstian slopes:

$$KS = \frac{E_B - E_A}{S_A} - \log a^{(S_B/S_A - 1)} \qquad (26)$$

where S_B and S_A are the measured calibration slopes for the two ions, and E_B and E_A are the measured potentials when the ions are present in pure solution at an activity equal to a. The values of KS calculated in this manner are far less dependent on activity than those calculated using the Nicolsky equation.

Liteanu and co-workers (43) have applied statistical analysis, taking into account fluctuations in the signal, to the measurement of selectivity. They obtain an expression for a selectivity coefficient β:

$$\beta = \left(\frac{C_A}{C_B}\right)_{P_{10},P_{11}} \tag{27}$$

where c_A and c_B are the concentrations of the interfering and primary ion respectively for which there is a probability of P_{11} that the interfering ion affects the primary ion signal and a probability of P_{10} that it does not. On the basis of statistical calculations of β for both separate solutions and mixed solutions, they have concluded that the values of β obtained from separate solution data will be different from those obtained from mixed solution data, and that only mixed solution data should be used.

In addition to devising these various methods for the measurement of selectivity, a considerable amount of work, both theoretical and experimental, has been done to identify the parameters (such as ionic mobilities, partition coefficients and equilibrium constants) which contribute to the

value of the selectivity coefficient. Bagg and co-workers (44,45) have used the Eisenman model to calculate an expression for the response of a liquid membrane electrode, based on the calcium salt of dodecylphosphoric acid (ddp), to a monovalent cation M^+. The final expression is of the same form as the Nicolsky equation, with a selectivity parameter K_m equal to

$$K_m = \left\{ \frac{K_{12s}(K_{2s})^2 \gamma_{Ca}}{(K_{1s})^{4/3} (2\bar{c})^{1/3} \gamma_m^2} \right\}^{1/2} \quad (28)$$

where γ refers to a single ion activity coefficient in the membrane, $\bar{c}$ is the concentration of the $Ca(ddp)_2$ salt in the membrane, and K_{1S}, K_{2S} and K_{12S} are the equilibrium constants for the following reactions:

$$Ca(ddp)_2 \rightleftarrows Ca^{2+} + 2\ ddp^-;\ K_{1s} \quad (29)$$

$$M(ddp) \rightleftarrows M^+ + ddp^-;\ K_{2s} \quad (30)$$

$$Ca(ddp)_2 + 2\ M^+ \rightleftarrows 2\ M(ddp) + Ca^{2+};\ K_{12s} \quad (31)$$

Danesi and co-workers (46) have shown that the selectivity of an organic cationic exchanger for one anion over another is given by

$$k^{pot}_{A,B} = K_A u_A / K_B u_B \quad (32)$$

where K is the distribution constant and u is mobility. They point out that both the ratio u_A/u_B and the values of K_A and K_B may be dependent upon the concentration of the exchanger, as a result of its effect on the dielectric constant.

Fujinaga, Okazaki and Hara (47, 48) have shown that

the selectivity of a liquid ion-exchanger electrode based on an organic sulfonate or benzoate can be improved drastically by the addition of an alkylphenol to the membrane. They assume a case of strong association, using the Eisenman model, so that the selectivity coefficient is given by

$$k^{pot}_{A,B} = u_{SB}K_{SB}k_B/u_{SA}K_{SA}k_A \qquad (33)$$

where u_{SB} and u_{SA} are mobilities of the exchanger-ion pairs in the membrane, K_{SA} and K_{SB} are the ion pair dissociation constants, and k_B and k_A are the single ion partition coefficients. The single ion partition coefficients can be correlated with the free energy of transfer of the ion from water to the membrane, which is dependent upon the energy of hydration of the ion in water and its energy of solvation in the membrane. The presence of the alkylphenol apparently increases the solvation energy as a result of hydrogen bonding between the alkylphenol and the ion; the size of the increase depends upon the strength of the conjugate acid of the ion.

Bäck and Sandblom (49) and James, Carmack and Freiser (50) have examined the effect of solvent extraction parameters on the selectivity of ion-exchange type electrodes. Using the Eisenman model, Bäck and Sandblom obtained an expression for the selectivity coefficient in terms of the extraction constants, E_{QX_A} and E_{QX_B}, for the two ions A and B:

$$k^{pot}_{A,B} = (E_{QX_A}/E_{QX_B})^{1/2} \qquad (34)$$

The extraction constants are equal to the concentration of the ion pair QX in the organic phase (the membrane) divided by the concentration of the extractant Q and ion X in the aqueous phase. James et al. (50) have shown that the extraction constants do indeed correlate with measured selectivity constants.

Eyal and Rechnitz (51,52) have studied the selectivity of valinomycin-based and cyclic polyether-based neutral carrier electrodes. They measured the formation constants for several valinomycin/monovalent cation complexes in water/methanol mixtures, and compared the ratio of the formation constants for the cation complexes to the measured selectivity coefficient, finding reasonably good agreement. They concluded that the selectivity of the valinomycin-based electrode depended only on the formation constants in the aqueous phase and not on any membrane phase characteristics. They repeated these experiments using cyclic polyethers, in a 50% tetrahydrofuran/50% water mixture, and again found good agreement between the formation constants and the selectivity coefficients.

Yasaka and co-workers (53) have also studied the cyclic polyethers, in particular those which are chiral and show enantiomer selectivity, and have concluded that the selectivity depends primarily on the selectivity of the complex formation, which in turn appears to be dependent on the presence of bulky chiral side chains on the cyclic polyether.

The Morf model for neutral carriers predicts that selectivity is dependent on the partition coefficient for the complex. The partition coefficient is in turn a function of the charge on the ion and of the dielectric constant of the membrane. The selectivity coefficient $k^{pot}_{A,B}$ is then given by

$$\log k^{pot}_{A,B} = \text{constant} + \frac{2\alpha}{2r}\left(\frac{1}{\varepsilon}\right) \qquad (35)$$

where 2r is the overall diameter of the complex, α is a constant for a given complex and ε is the dielectric constant. Fiedler (54) has studied the effect of the dielectric constant on the selectivity of neutral carrier-type electrodes selective for sodium and calcium. The dielectric constant was varied by varying the relative amounts of two solvents used as the plasticizer in a PVC membrane containing the neutral carrier. The selectivity coefficients were found to vary in the manner predicted by theory, with selectivity for monovalent cations over divalent cations, and for large cations over smaller ones of the same charge, being favored by decreasing dielectric constants.

Morf and co-workers (55) have tabulated the theoretical expressions for the selectivity factor. In general the selectivity of a liquid membrane electrode is predicted from theory to depend upon the mobilities of the ions in the membrane and the partition coefficient of the ions between the external solution and the membrane. For liquid ion-

exchangers where there is a high degree of association, and for neutral carriers where there is in addition a dependence on the equilibrium constant for the displacement of the primary ion by the interfering ion in a complex, any factor, such as dielectric constant or solvation energy, which can alter the mobility, partition coefficient or equilibrium constant, can also be expected to affect selectivity.

CHAPTER 4
OBJECTIVES AND OVERVIEW OF THE WORK

It has been noted by several researchers (40-42, 56, 57) that the values of the selectivity coefficient determined using the Nicolsky equation may vary considerably as the activity of the test solutions is varied. It was decided to explore this activity dependence in more depth in this present work with the goal of characterizing the pattern of the activity dependence, attempting to identify the cause, and determining which of the various measurement methods produces the least activity dependence.

For this work a neutral carrier-type electrode based on the ligand Anal-05, whose structure is shown in Figure 3, was chosen. This ligand had previously been used by Pungor's group in Budapest, and was known to be responsive to calcium in preference to the other alkaline earth or alkali metals, but also to give activity-dependent selectivity coefficients by both the separate solution and mixed solution methods. It was also known from Fiedler's work (54) that the selectivity of electrodes of this type could be varied by changing the composition of the plasticizer. This is important since it is necessary that the selectivity coefficient be in the range of 0.01 to 1, so that two good

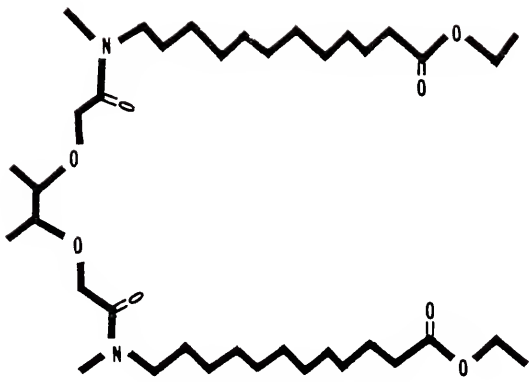

FIGURE 3. Structure of the Ligand Anal-05.

linear portions can be obtained in the graphical mixed solution method. A placticizer composition of 0.8 mole fraction dibutyl sebacate and 0.2 mole fraction o-nitrophenyl-n-octyl ether was chosen, which gave an acceptable selectivity for calcium over barium.

The selectivity coefficient, $k^{pot}_{Ca,Ba}$, was then measured by both the separate solution and mixed solution methods, over a wide range of activities. It became apparent early on that the response of the electrode was not Nernstian, in that the slope of the response to either calcium or barium was lower than the Nernstian value of 29.5 mV per decade activity change, and in addition the response of the electrode to barium deviated somewhat from linearity. The linearity problem was handled by simply using only those data points which approximated linearity, as judged both visually and by the value of the correlation coefficient obtained from linear regression analysis. An attempt was made to correct, or modify, the Nicolsky equation to include the measured slopes; this yielded an equation similar to that previously reported by Mohan and Rechnitz (41) and Hakoila and co-workers (42). The derivation of this equation is as follows:

1. The two ions, A and B with charges z_A and z_B respectively, exhibit linear calibration curves with slopes of S_A and S_B and intercepts of E^o_A and E^o_B. The following

two equations are then valid.

$$E_A = E_A^o + S_A \log a_A \quad (36)$$

$$E_B = E_B^o + S_B \log a_B \quad (37)$$

2. The response to ion B may be expressed in terms of the slope and intercept for ion A, using a selectivity parameter $k^R_{A,B}$ which is defined as follows:

$$\log K^R_{A,B} = (E_B^o - E_A^o)/S_A \quad (38)$$

Eqn. 37 then becomes

$$E_B = E_A^o + S_A \log (k^R_{A,B}\, a_B^{(S_B/S_A)}) \quad (39)$$

3. In the separate solution method using approximately equal activities it is the two potentials, E_A and E_B, that are compared. Subtracting Eqn. 36 from Eqn. 39 one obtains

$$E_B - E_A = S_A \log (k^R_{A,B} a_B^{(S_B/S_A)}/a_A) \quad (40)$$

4. The corresponding Nicolsky equation for the situation in which the experimental slope is used for ion A but it is assumed that the ratio of slopes is equal to the ratio of the charges on the ions is as follows:

$$E_B - E_A = S_A \log (k^{pot}_{A,B}\, a_B^{(Z_A/Z_B)}/a_A) \quad (41)$$

Comparing this to Eqn. 40 it can be shown that the selectivity coefficient $k^R_{A,B}$ calculated using experimental slopes bears the following relationship to $k^{pot}_{A,B}$:

$$\log k^R_{A,B} = \log k^{pot}_{A,B} + (Z_A/Z_B - S_B/S_A) \log a_B \quad (42)$$

5. In the mixed solution graphical cross-point method it is the potentials which are equal, at the cross-point.

Thus:

$$E_A^o + S_A \log a_A = E_A^o + S_A \log (k_{A,B}^{XPR} a_B^{(S_B/S_A)}) \quad (43)$$

$$k_{A,B}^{XPR} = a_A/a_B^{(S_B/S_A)} \quad (44)$$

The corresponding form of the Nicolsky equation is

$$E_A^o + S_A \log a_A = E_A^o + S_A \log (k_{A,B}^{XP} a_B^{(Z_A/Z_B)}) \quad (45)$$

By comparison of Eqns. 43 and 45 it can be shown that Eqn. 42 holds in this case also.

Values of $k_{A,B}^{R}$ were computed for the Anal-05 electrode, and were found to be virtually independent of activity in the region of linear response.

Having shown that, through use of measured slopes rather than Nernstian slopes, a selectivity parameter could be obtained which was independent of activity, attention was turned to determining which of the methods--separate or mixed solution, Nernstian or real slope--gave the most accurate description of the electrode response. For this part of the study two additional electrodes were selected. In view of Morf's contention (55) that the response of an electrode to a mixture of monovalent and divalent cations does not obey the simple Nicolsky equation, it was decided to examine an electrode based on a ligand responsive to both a monovalent and a divalent cation. An electrode based on the ligand AC-14/81, whose structure is shown in Figure 4, was chosen. This ligand responds primarily to sodium ion, but also responds to calcium ion. In addition, in view of

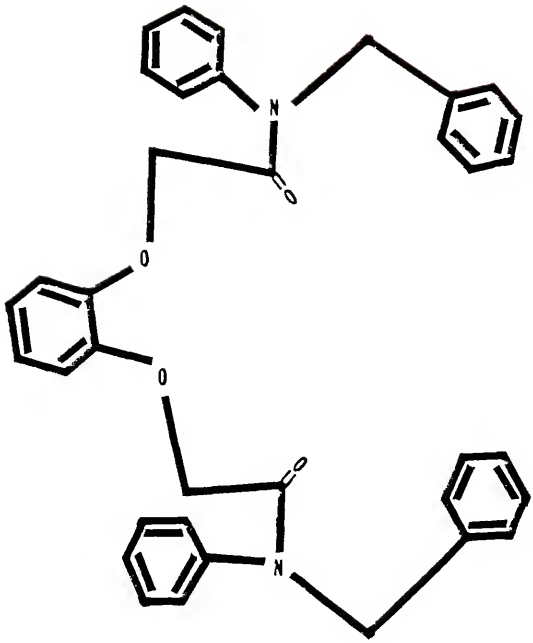

FIGURE 4. Structure of the Ligand AC-14/81.

Buck's suggestion that non-Nernstian behavior is a result of Donnan Exclusion failure (26-32), it was decided to examine an electrode based on a charged liquid ion-exchanger, rather than a neutral carrier, since in this type of electrode the presence of a charged ion-exchanger in the membrane would be expected to affect the ability of co-ions to penetrate the membrane. A commercially available electrode, the Corning calcium-selective electrode, was chosen. Selectivity coefficients were measured by both the separate and the mixed solution methods, using both measured and Nernstian slopes. These selectivity coefficients were then used to predict the potentials that would be exhibited by the electrode in various mixed solutions, and these were compared to the actual measured potentials. The results of these experiments are given in the next chapters.

CHAPTER 5
SEPARATE SOLUTION MEASUREMENTS

Neutral Carrier Electrode Based on Anal-05

Experimental System

As mentioned earlier, the first set of experiments involved a neutral carrier electrode based on the ligand Anal-05, or N,N' di [(11-ethoxycarbonyl) undecyl]-N,N', 4,5-tetramethyl-3,6-dioxaoctane amide. The Anal-05 was incorporated in a membrane prepared by dissolving approximately 5 mg of Anal-05, 45 mg of polyvinyl chloride (PVC) powder and about 100 mg of plasticizer (a mixture of dibutyl sebacate and o-nitrophenyl-n-octyl ether, with a mole fraction of dibutyl sebacate of 0.8) in two to three ml of tetrahydrofuran. This solution was poured into a 28-mm diameter glass ring and allowed to evaporate at room temperature to produce a membrane of about 0.5 mm thickness, which was then cut into 7-mm diameter circles using a cork borer. Two of these 7-mm diameter circles were incorporated into NV Philips ion-selective electrode bodies, using a 0.01 M $CaCl_2$ internal filling solution, to produce two electrodes given the code names G1 and G2. These electrodes were soaked in 0.001 M $CaCl_2$ for several days before use.

The potentials of these electrodes in test solutions containing $CaCl_2$ and/or $BaCl_2$ were measured relative to a

Radelkis OP-0820P Ag/AgCl electrode with a 1 M KCl filling solution; the cell short-hand notation is given below.

Ag/AgCl, 1M KCl//test solution/PVC membrane/0.01 M $CaCl_2$/internal metal contact

All potential measurements were made using a Radiometer PHM 64 Research pH Meter. The electrodes and test solution were placed in a water-jacketed cell, and the temperature was kept at 25.0±0.1°C using a circulating constant-temperature bath. During measurements the test solution was stirred using a magnetic stirrer. A diagram of the apparatus is shown in Figure 5.

In this portion of the work ten different concentrations of pure solutions of $CaCl_2$ and of $BaCl_2$ were used; these are given in Table 2. The solutions were prepared by consecutively adding small amounts of 0.1 M and 1 M solutions of either $BaCl_2$ or $CaCl_2$ to a known volume of an initially 10^{-5} M solution of the same salt. The volumes added were measured using either a Radelkis OP-930 Automatic Burette or a Dispensette bottle buret, both of which had been previously calibrated. In this way a large number of concentrations could be prepared in a single container and the electrode potentials measured in them, in a relatively short period of time. The entire set of measurements was repeated on six successive days.

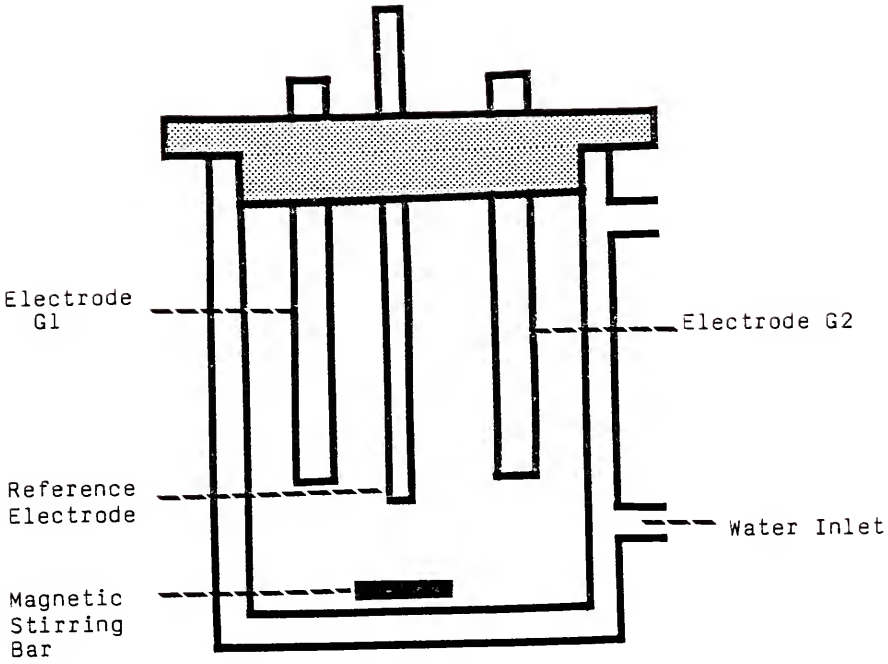

FIGURE 5. Apparatus for Potential Measurements Using Electrodes G1 and G2.

TABLE 2
CONCENTRATIONS OF $CaCl_2$ AND $BaCl_2$ PURE SOLUTIONS

1.000×10^{-5} M

1.083×10^{-4} M

2.896×10^{-4} M

4.702×10^{-4} M

8.294×10^{-4} M

1.891×10^{-3} M

3.613×10^{-3} M

6.878×10^{-3} M

2.493×10^{-2} M

4.234×10^{-2} M

Data Treatment

For each of the solutions used, mean activity coefficients were calculated for the calcium or barium salt, as appropriate, using a two parameter Debye-Hückel equation (58):

$$\log \gamma_{\pm} = \frac{-0.509 \mid Z_+Z_- \mid \sqrt{I}}{1 + 0.328A\sqrt{I}} + cI \qquad (46)$$

where z_+ is the charge on the cation, z_- is the charge on the anion, I is the ionic strength, and A and c are parameters which are experimentally determined to give the closest fit to measured mean activity coefficients. Individual ion activity coefficients for Ca^{2+} and Ba^{2+} were calculated using the convention (59)

$$\log \gamma_+ = \left| \frac{z_+}{z_-} \right| \log \gamma_{\pm} \qquad (47)$$

The concentrations of the salt solutions were then converted to activities of calcium or barium ion using these single-ion activity coefficients.

The measured potentials include a contribution due to the liquid-junction potential at the reference electrode (1M KCl)/test solution interface. This liquid-junction, or diffusion potential, E_d, was calculated using a form of the Henderson equation, given below, and subtracted from each measured potential to obtain the corrected potential needed for the calculation of the selectivity coefficient.

$$E_d = \frac{\sum_n z_n u_n (c_n' - c_n'')}{\sum_n z_n^2 u_n (c_n' - c_n'')} \frac{RT}{F} \ln \frac{\sum_n z_n^2 u_n c_n'}{\sum_n z_n^2 u_n c_n''} \quad (48)$$

Here n refers to any ion, positive or negative, present in the solution; z, u and c refer to the charge, mobility and concentration of the ion, and the ' and " refer to the reference electrode and test solution respectively. The activities and corrected potentials for electrodes G1 and G2 are given in Table 3 for the six days on which measurements were made.

Calibration plots were prepared using these data; a typical plot is shown in Figure 6. As can be seen, the data at the low and high concentration ends vary somewhat from linearity; these points were omitted from all further calculations. Using the data in the linear region, response slopes and y-intercepts were calculated using the linear regression program "CURVE" supplied with the Hewlett-Packard HP-85 Computer.

The slope and intercept calculated for calcium on each day were used in the calculation of the Nicolsky selectivity coefficient, $k^{pot}_{Ca,Ba}$, using Eqn. 41. The results are given in Table 4, along with the standard deviation over both the time and the activity ranges involved. These values of $k^{pot}_{Ca,Ba}$ were then converted to values of $k^{R}_{Ca,Ba}$ using Eqn. 42. The results are given in Table 5.

TABLE 3
ACTIVITIES AND CORRECTED POTENTIALS FOR ELECTRODES G1 AND G2 IN $CaCl_2$ AND $BaCl_2$ SOLUTIONS

	Electrode G1			
Activity	EMF-1	EMF-2	EMF-3	EMF-4
9.75×10^{-6} M $CaCl_2$	23.6mV	35.3mV	31.9mV	37.2mV
1.00×10^{-4}	45.4	53.1	51.0	55.6
2.54×10^{-4}	57.2	62.8	60.9	65.6
3.99×10^{-4}	63.9	67.4	66.0	70.2
6.70×10^{-4}	71.1	73.5	72.1	75.8
1.38×10^{-3}	80.5	82.4	80.7	84.1
2.39×10^{-3}	89.5	89.5	87.4	90.5
4.02×10^{-3}	96.7	96.1	94.0	96.6
1.05×10^{-2}	110.1	108.2	106.5	108.2
1.51×10^{-2}	115.4	116.7	111.6	113.0
9.75×10^{-6} M $BaCl_2$	30.6mV	36.2mV	35.1mV	23.1mV
9.96×10^{-5}	36.8	42.3	41.7	31.2
2.54×10^{-4}	43.4	48.6	47.5	38.1
3.98×10^{-4}	46.1	51.6	50.3	41.9
6.67×10^{-4}	50.9	55.8	54.6	46.5
1.38×10^{-3}	58.2	62.4	60.6	53.6
2.36×10^{-3}	63.9	67.7	65.5	59.0
3.98×10^{-3}	70.1	73.0	70.5	64.5
1.00×10^{-2}	81.1	82.6	79.5	75.7
1.44×10^{-2}	85.9	87.1	83.7	80.8

Electrode G2

EMF-5	EMF-6	EMF-1	EMF-2	EMF-3	EMF-4	EMF-5	EMF-6
32.9mV	34.2mV	19.5mV	27.5mV	26.7mV	25.5mV	23.9mV	27.6mV
52.9	49.4	40.6	46.0	45.7	45.0	45.7	44.2
62.5	59.0	51.9	55.8	55.5	55.3	55.9	54.0
67.2	63.3	57.9	60.6	60.4	60.3	60.8	58.7
72.9	69.2	64.7	66.5	66.0	66.0	66.7	64.6
80.9	77.3	73.7	75.4	74.5	74.2	75.0	72.7
87.2	83.9	81.4	82.2	81.0	80.6	81.2	79.1
93.2	89.8	88.4	88.7	87.5	86.9	87.5	85.5
104.5	102.0	100.5	106.5	99.0	98.4	98.9	97.5
109.2	107.0	105.5	112.6	103.9	103.5	103.9	102.4
22.0mV	26.2mV	17.6	22.7	22.0	19.2	18.7	21.7
30.1	31.4	25.6	30.4	30.6	27.8	27.9	27.3
37.1	37.1	32.4	36.9	36.6	34.9	34.7	32.6
40.5	39.7	36.3	40.5	40.2	38.7	38.4	36.0
45.3	44.2	41.5	45.4	44.7	43.4	43.1	40.5
51.7	50.4	49.4	52.6	51.8	50.7	50.3	47.4
57.2	55.9	55.7	58.3	57.3	56.4	55.9	53.0
62.7	61.3	61.9	64.1	63.0	62.1	61.7	58.7
74.4	73.4	74.1	75.4	73.8	73.3	73.5	70.4
79.6	78.4	79.3	80.5	78.9	78.4	78.7	75.6

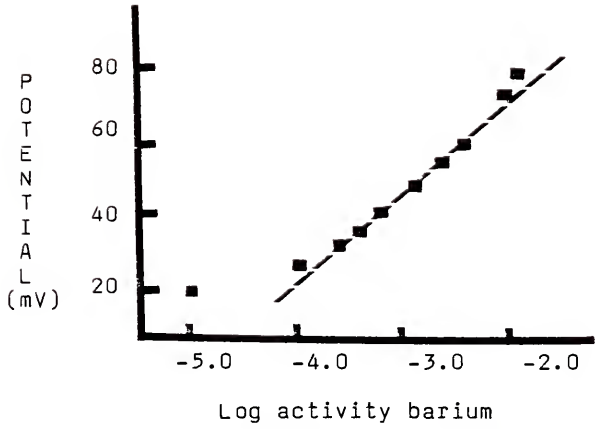

FIGURE 6. Calibration Plot for Electrode G2.

TABLE 4
SEPARATE SOLUTION SELECTIVITY COEFFICIENT $k^{pot}_{Ca,Ba}$
FOR ELECTRODES G1 AND G2

Concentration	DAY1	DAY2	DAY3	DAY4	DAY5	DAY6	S.D.[a]
Electrode G1							
4.702×10^{-4} M	.284	.269	.277	.0887	.0975	.136	.094
8.294×10^{-4}	.240	.229	.239	.0815	.0902	.121	.077
1.891×10^{-3}	.206	.188	.192	.0731	.0779	.102	.062
3.613×10^{-3}	.163	.162	.166	.0673	.0729	.0933	.048
6.878×10^{-3}	.153	.147	.146	.0643	.0701	.0899	.041
Standard[b] Deviation	.054	.050	.054	.010	.012	.020	
Electrode G2							
4.702×10^{-4} M	.194	.189	.184	.153	.149	.149	.022
8.294×10^{-4}	.172	.174	.167	.141	.135	.132	.020
1.891×10^{-3}	.157	.150	.148	.129	.122	.119	.016
3.613×10^{-3}	.142	.137	.136	.122	.116	.111	.013
6.878×10^{-3}	.134	.130	.128	.117	.112	.106	.011
Standard Deviation	.024	.025	.022	.014	.015	.017	

[a] Standard deviation of $k^{pot}_{Ca,Ba}$ (measured at the indicated concentration) over the six days.

[b] Standard deviation of $k^{pot}_{Ca,Ba}$ on the day indicated over the concentration range.

TABLE 5

SEPARATE SOLUTION SELECTIVITY COEFFICIENT $k^{R}_{Ca,Ba}$ FOR ELECTRODES G1 AND G2

Concentration	DAY1	DAY2	DAY3	DAY4	DAY5	DAY6	S.D.[a]
Electrode G1							
4.702×10^{-4} M	.0432	.0581	.0366	.0415	.0506	.0511	.0078
8.294×10^{-4}	.0413	.0547	.0359	.0401	.0489	.0485	.0070
1.891×10^{-3}	.0422	.0514	.0349	.0386	.0449	.0448	.0057
3.613×10^{-3}	.0380	.0496	.0347	.0374	.0440	.0438	.0055
6.878×10^{-3}	.0404	.0498	.0349	.0376	.0442	.0450	.0054
Standard[b] Deviation	.0020	.0036	.0095	.0017	.0030	.0029	
Electrode G2							
4.702×10^{-4}	.0826	.0879	.0736	.0952	.0429	.0316	.026
8.294×10^{-4}	.0776	.0851	.0710	.0905	.0423	.0310	.026
1.891×10^{-3}	.0766	.0788	.0685	.0866	.0428	.0322	.022
3.613×10^{-3}	.0734	.0758	.0670	.0845	.0443	.0335	.020
6.878×10^{-3}	.0734	.0757	.0671	.0837	.0465	.0355	.019
Standard Deviation	.0038	.0056	.0028	.0048	.0017	.0018	

[a] Standard deviation of $k^{R}_{Ca,Ba}$ (measured at the indicated concentration) over the six days.

[b] Standard deviation of $k^{R}_{Ca,Ba}$ on the day indicated over the concentration range.

Neutral Carrier Electrode Based on AC-14/81

Experimental System

In the second set of experiments a neutral carrier electrode using the ligand AC-14/81, which is selective for sodium but also responds to calcium, was used. The membrane was prepared in the same manner as that using Anal-05; the membrane composition was approximately 2 mg of AC-14/81, 48 mg of PVC powder and 100 mg of o-nitrophenyl-n-octyl ether. Two electrodes, Q1 qnd Q2, were prepared, with 0.01 M NaCl as the internal filling solution. The electrodes were soaked in 0.01 M NaCl prior to use.

The reference electrode was again a Radelkis Ag/AgCl electrode, but with a 0.1 M lithium acetate filling solution. The short-hand cell notation is

Ag/AgCl,0.1M $LiC_2H_3O_2$//test solution/PVC membrane/
0.01 M NaCl/ internal contact

A Radiometer PHM 84 Research pH Meter was used for the potential measurements. The electrodes and test solution were placed in a measuring cell which consisted of a beaker cut flat at the top and a plastic cap with holes drilled to accommodate the electrodes and a paddle-type mechanical stirrer. The entire cell was placed in a constant-temperature bath, and the temperature was maintained at 25.0±0.1°C. A diagram of the apparatus is shown in Figure 7.

Eight concentrations of sodium chloride and of calcium chloride were used, ranging from 9×10^{-5} to 7×10^{-2} M.

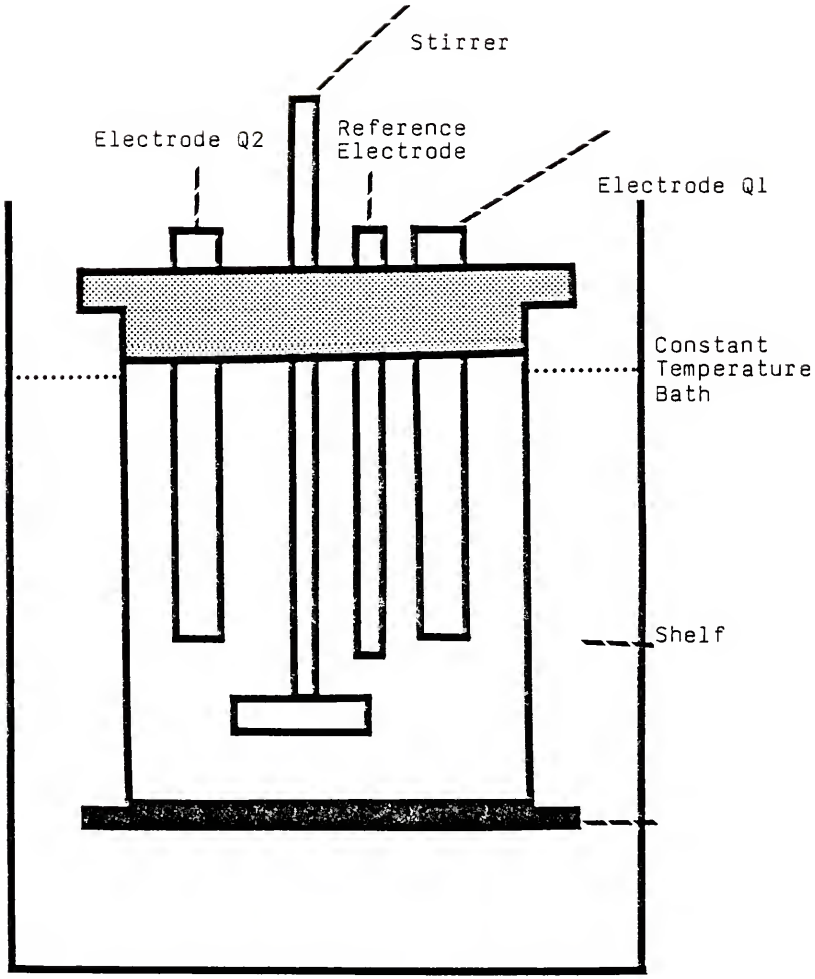

FIGURE 7. Apparatus for Potential Measurements Using Electrodes Q1 and Q2.

These solutions were prepared in the same manner as those used in the first set of experiments. Measurements were repeated on 12 days.

Single-ion activity coefficients were calculated for sodium or calcium in each solution using Eqns. 46 and 47, and diffusion potentials using Eqn. 48. Activities and corrected potentials were then calculated; these are given in Tables 6 and 7 for the twelve days on which measurements were made.

Once again some non-linearity was observed, especially for the interfering ion, calcium. As in the first set of experiments points deviating from linearity were deleted before calculation of the linear regression line. The values of $k^{pot}_{Na,Ca}$ and $k^{R}_{Na,Ca}$ were calculated from Eqns. 41 and 42; these are shown in Tables 8 and 9.

Ion-Exchange Electrode for Calcium Ion

Experimental System

In the third set of measurements a Corning ion-exchange type electrode, selective for calcium but also responsive to barium, was used. A Fisher Ag/AgCl Inverted Sleeve Junction reference electrode was used, with 1 M KCl as the filling solution. The short-hand cell notation is

Ag/AgCl, 1 M KCl//test solution/Corning electrode

The calcium electrode was soaked in 0.01 M calcium chloride before use.

The apparatus used was similar to that used in the

TABLE 6
ACTIVITIES AND CORRECTED POTENTIALS FOR
ELECTRODE Q1 IN NaCl AND $CaCl_2$ SOLUTIONS

Activity	EMF-1	EMF-2	EMF-3	EMF-4	EMF-5
2.771×10^{-4} M NaCl	-42.3mV	-42.7mV	-44.0mV	-44.5mV	-44.5mV
4.585×10^{-4}	-32.7	-33.1	-33.8	-34.4	-34.7
8.157×10^{-4}	-20.9	-22.6	-22.2	-23.4	-23.6
1.853×10^{-3}	-3.0	-4.7	- 3.6	- 4.6	- 4.9
3.630×10^{-3}	10.8	7.6	10.5	9.1	9.0
2.296×10^{-4} M $CaCl_2$	-65.6	-66.4	-60.8	-61.8	-64.5
3.691×10^{-4}	-61.9	-62.4	-57.1	-57.9	-60.7
6.299×10^{-4}	-57.7	-58.0	-53.3	-54.7	-57.2
1.319×10^{-3}	-50.5	-51.2	-45.9	-47.6	-50.0
2.366×10^{-3}	-44.6	-46.0	-40.1	-41.7	-44.3

EMF-6	EMF-7	EMF-8	EMF-9	EMF-10	EMF-11	EMF-12
-43.8mV	-44.5mV	-47.4mV	-48.8mV	-47.1mV	-48.8mV	-51.7mV
-34.3	-35.7	-37.3	-38.8	-37.3	-39.5	-41.7
-23.0	-24.7	-25.7	-26.9	-26.1	-29.0	-29.5
-4.8	-7.2	-7.4	-8.6	-7.8	-10.8	-11.1
8.0	5.7	6.8	5.4	6.3	2.4	3.4
-64.6	-64.2	-67.8	-70.6	-71.3	-73.2	-74.6
-61.0	-60.6	-64.4	-67.0	-68.4	-69.3	-72.9
-57.4	-56.8	-60.2	-62.9	-66.2	-65.8	-70.2
-49.8	-49.4	-53.4	-55.7	-59.2	-58.4	-63.6
-44.0	-43.6	-47.7	-50.7	-54.0	-52.5	-57.2

TABLE 7
ACTIVITIES AND CORRECTED POTENTIALS FOR ELECTRODE Q2
IN NaCl AND $CaCl_2$ SOLUTIONS

Activity	EMF-1	EMF-2	EMF-3	EMF-4	EMF-5
2.771×10^{-4} M NaCl	-40.3mV	-41.7mV	-33.3mV	-34.5mV	-38.8mV
4.585×10^{-4}	-30.8	-32.4	-23.5	-25.2	-30.1
8.157×10^{-4}	-18.6	-20.7	-11.8	-14.7	-18.2
1.853×10^{-3}	-1.2	-3.5	5.9	2.8	-0.1
3.630×10^{-3}	13.2	10.7	19.8	16.2	14.3
2.296×10^{-4} M $CaCl_2$	-59.5	-58.6	-50.2	-53.1	-54.4
3.691×10^{-4}	-56.0	-54.7	-47.4	-49.8	-51.4
6.299×10^{-4}	-51.2	-49.7	-42.9	-45.3	-46.4
1.319×10^{-3}	-44.3	-43.4	-36.1	-39.4	-40.3
2.366×10^{-3}	-37.3	-37.6	-30.2	-32.7	-33.5

EMF-6	EMF-7	EMF-8	EMF-9	EMF-10	EMF-11
-39.0mV	-39.0mV	-39.3mV	-40.4mV	-39.6mV	-47.8mV
-29.2	-30.5	-28.9	-30.6	-29.6	-38.0
-17.1	-18.6	-16.7	-18.0	-17.4	-26.4
0.9	-1.3	1.8	0.2	0.7	-8.4
14.3	12.9	16.4	15.1	15.1	6.1
-51.9	-53.4	-52.7	-55.8	-56.5	-60.1
-49.2	-50.6	-49.9	-52.4	-55.4	-55.0
-44.7	-45.6	-45.0	-47.5	-50.8	-50.9
-38.1	-38.7	-38.4	-40.4	-44.7	-44.0
-31.3	-32.0	-31.9	-34.1	-37.9	-37.7

TABLE 8
SEPARATE SOLUTION SELECTIVITY COEFFICIENTS $k^{pot}_{Na,Ca}$ FOR ELECTRODES Q1 AND Q2

Concentration	DAY1	DAY2	DAY3	DAY4	DAY5	DAY6
Electrode Q1						
2.825×10^{-4} M	.00597	.00552	.00832	.00803	.00705	.00659
4.700×10^{-4}	.00586	.00541	.00800	.00778	.00691	.00643
8.428×10^{-4}	.00555	.00543	.00757	.00732	.00656	.00768
1.945×10^{-3}	.00520	.00485	.00702	.00657	.00595	.00560
3.882×10^{-3}	.00521	.00495	.00696	.00663	.00588	.00581
Standard Deviation	.00036	.00031	.00060	.00066	.00054	.00082
Relative Std. Dev.	6.4%	5.9%	7.9%	9.1%	8.3%	12.7%
Electrode Q2						
2.825×10^{-4} M	.00731	.00801	.00811	.00717	.00867	.00988
4.700×10^{-4}	.00716	.00802	.00754	.00691	.00860	.00917
8.428×10^{-4}	.00686	.00788	.00728	.00696	.00844	.00871
1.945×10^{-3}	.00651	.00726	.00675	.00609	.00745	.00792
3.882×10^{-3}	.00669	.00704	.00671	.00635	.00757	.00845
Standard Deviation	.00033	.00046	.00058	.00045	.00059	.00074
Relative Std. Dev.	4.8%	6.0%	8.0%	6.8%	7.2%	8.4%

DAY7	DAY8	DAY9	DAY10	DAY11	DAY12
.00675	.00699	.00656	.00575	.00544	.00632
.00676	.00664	.00632	.00538	.00542	.00560
.00641	.00639	.00597	.00477	.00522	.00492
.00603	.00583	.00556	.00436	.00479	.00446
.00616	.00570	.00532	.00416	.00487	.00448
.00033	.00054	.00051	.00067	.00030	.00080
5.2%	8.6%	8.7%	13.8%	5.9%	15.5%

.00903	.00989	.00901	.00830	.0102
.00889	.00909	.00874	.00713	.0106
.00865	.00886	.00837	.00682	.0102
.00814	.00805	.00787	.00610	.00942
.00823	.00811	.00774	.00625	.00933
.00039	.00076	.00055	.00088	.00055
4.6%	8.6%	6.5%	12.7%	5.5%

TABLE 9

SEPARATE SOLUTION SELECTIVITY COEFFICIENTS $k^{R}_{Na,Ca}$ FOR ELECTRODES Q1 AND Q2

Concentration	DAY1	DAY2	DAY3	DAY4	DAY5	DAY6
2.825×10^{-4} M	.00344	.00345	.00417	.00371	.00337	.000382
4.700×10^{-4}	.00348	.00347	.00417	.00376	.00345	.000385
8.428×10^{-4}	.00342	.00359	.00412	.00371	.00343	.000476
1.945×10^{-3}	.00336	.00334	.00406	.00357	.00332	.000364
3.882×10^{-3}	.00350	.00353	.00423	.00380	.00345	.000392
Standard Deviation	.00005	.00009	.00006	.00009	.00006	.000038
Relative Std. Dev.	1.6%	2.7%	1.5%	2.3%	1.7%	11.0%
Electrode Q2						
2.825×10^{-4} M	.00490	.00482	.00409	.00417	.00475	.00519
4.700×10^{-4}	.00491	.00497	.00396	.00415	.00488	.00500
8.428×10^{-4}	.00483	.00504	.00399	.00432	.00497	.00495
1.945×10^{-3}	.00474	.00486	.00393	.00397	.00463	.00476
3.882×10^{-3}	.00501	.00488	.00410	.00430	.00491	.00531
Standard Deviation	.00010	.00009	.00008	.00014	.00014	.00021
Relative Std. Dev.	2.1%	1.8%	1.7%	3.4%	2.8%	4.2%

DAY7	DAY8	DAY9	DAY10	DAY11	DAY12
.00438	.00323	.00301	.00171	.00331	.00178
.00449	.00320	.00303	.00172	.00339	.00169
.00438	.00324	.00301	.00164	.00337	.00161
.00428	.00316	.00300	.00167	.00323	.00164
.00451	.00326	.00303	.00174	.00340	.00180
.00009	.00004	.00001	.00004	.00007	.00008
2.1%	1.2%	0.4%	2.4%	2.1%	4.9%

.00615	.00478	.00510	.00309	.00645
.00619	.00458	.00511	.00281	.00688
.00617	.00467	.00507	.00286	.00682
.00601	.00453	.00501	.00279	.00656
.00624	.00480	.00513	.00306	.00671
.00009	.00012	.00005	.00014	.00018
1.4%	2.5%	0.9%	4.9%	2.7%

second set of experiments and consisted of a beaker with a plastic cap designed to accommodate the electrodes and a paddle-type stirrer. It was observed that the stirrer caused noise in the potential response; as a result the stirrer was turned off during measurements. The beaker was placed in a constant-temperature bath maintained at $25.0 \pm 0.1^{o}C$. A Corning Model 190 pH Meter was used for all potential measurements, and a Sargent-Welch Model SRG Recorder was used to record the response of the electrodes, which was rather slow and often required ten minutes or longer to reach a stable potential.

Seven concentrations of calcium chloride and of barium chloride were used, ranging from 10^{-5} M to 0.01 M. These were prepared in a manner analogous to that previously used. The measurements were repeated on five days.

Data Treatment

Once again non-linearity was observed at the low and high concentrations ends, and these data points were omitted from the calculations. Activity coefficients and diffusion potentials were again calculated using Eqns. 46-48; activities and corrected potentials are given in Table 10. Values of $k^{pot}_{Ca,Ba}$ and $k^{R}_{Ca,Ba}$ were calculated; these are given in Table 11.

TABLE 10
ACTIVITIES AND CORRECTED POTENTIALS FOR THE CORNING ELECTRODE IN $CaCl_2$ AND $BaCl_2$ SOLUTIONS

Activity	EMF-1	EMF-2	EMF-3	EMF-4	EMF-5
9.96×10^{-5}M $CaCl_2$	56.7mV	57.1mV	56.2mV	55.6mV	55.2mV
4.95×10^{-4}M	77.7	77.5	76.4	76.1	75.4
8.46×10^{-4}	85.0	84.8	83.8	83.0	82.9
3.54×10^{-3}	104.4	102.4	102.9	102.6	101.9
9.96×10^{-5}M $BaCl_2$	27.3	23.4	24.0	23.2	27.4
4.94×10^{-4}	34.2	30.4	30.7	29.3	31.9
8.43×10^{-4}	34.1	31.9	31.3	29.8	34.0
3.50×10^{-3}	41.5	38.3	39.8	35.6	40.2

TABLE 11

SEPARATE SOLUTION SELECTIVITY COEFFICIENTS $k^{pot}_{Ca,Ba}$ AND $k^{R}_{Ca,Ba}$ FOR THE CORNING ELECTRODE

	$k^{pot}_{Ca,Ba}$				
Concentration	Day 1	Day 2	Day 3	Day 4	Day 5
1.08×10^{-4} M	.110	.0701	.0852	.0852	.119
5.95×10^{-4}	.0384	.0244	.0304	.0286	.0360
1.08×10^{-3}	.0220	.0155	.0181	.0176	.0238
5.90×10^{-3}	.00904	.00645	.00810	.00622	.00902
Standard Deviation	.0451	.0283	.0344	.0351	.0493
Relative Std. Dev.	100%	97.2%	97.0%	102%	105%
	$k^{R}_{Ca,Ba}$				
1.08×10^{-4} M	.000158	.000144	.000181	.000094	.000150
5.95×10^{-4}	.000172	.000147	.000188	.000103	.000145
1.08×10^{-4}	.000144	.000134	.000160	.000094	.000141
5.90×10^{-3}	.000163	.000145	.000186	.000095	.000150
Standard Deviation	.000012	.000006	.000013	.000004	.000004
Relative Std. Dev.	7.35%	4.07%	7.18%	4.52%	2.98%

CHAPTER 6
MIXED SOLUTION MEASUREMENTS

Neutral Carrier Electrode Based on Anal-05

Experimental System

The experimental apparatus has already been described. The mixtures of calcium chloride and barium chloride were prepared in a manner analogous to that used in the preparation of the pure solutions. Initially a solution was prepared containing one salt at 10^{-5} M and the other salt at a higher concentration. The concentration of the first salt was then increased by adding small volumes of 0.1 M or 1 M solutions of that salt. For example, a solution containing 10^{-5} M calcium chloride was prepared, 50 ml of this transferred into the cell by pipette, and the concentration of barium chloride varied by adding 0.1 M or 1 M barium chloride to the cell. On days 1-3 the concentration of barium was varied, leaving the calcium concentration fixed at one of seven levels, while on days 4-6 the calcium concentration was varied, with the barium concentration fixed at one of the five levels. The concentrations used are given in Table 12.

TABLE 12
CONCENTRATIONS USED IN $CaCl_2/BaCl_2$ MIXTURES

Fixed-ion Concentrations	Varied-ion concentrations
9.10×10^{-5} M $CaCl_2$	1.000×10^{-5} M
2.73×10^{-4}	1.083×10^{-4}
4.55×10^{-4}	2.064×10^{-4}
6.37×10^{-4}	3.043×10^{-4}
9.10×10^{-4}	4.020×10^{-4}
2.73×10^{-3}	7.616×10^{-4}
4.55×10^{-3}	1.296×10^{-3}
	2.001×10^{-3}
9.10×10^{-4} M $BaCl_2$	2.694×10^{-3}
2.73×10^{-3}	3.378×10^{-3}
4.55×10^{-3}	4.387×10^{-3}
6.37×10^{-3}	6.117×10^{-3}
9.10×10^{-3}	7.840×10^{-3}
	9.558 x 10-3
	1.297×10^{-2}
	1.805×10^{-2}
	2.641×10^{-2}
	3.462×10^{-2}
	4.270×10^{-2}
	5.064×10^{-2}

Data Treatment

Activity coefficients and diffusion potentials were calculated as for the separate solution measurements; activities and corrected potentials are given in Table 13 and Appendix A.

The data for the mixed solutions were plotted and the activity of the ion whose concentration was varied was determined at the cross-point, as shown in Figure 8. The activity of the ion whose concentration was fixed was determined by interpolation, as shown in Figure 9. The values of the selectivity coefficient, $k^{pot}_{Ca,Ba}$, were then calculated using Eqn. 45; they are shown in Table 14 along with the standard deviations. The values of $k^{pot}_{Ca,Ba}$ were converted to values of $k^{R}_{Ca,Ba}$ using Eqn. 42; these are also given in Table 14.

The mixed solution data were also treated using a multi-parametric curve-fitting program, "SELECT", available at the Technical University of Budapest. This program varies the values of S, K ($k^{pot}_{A,B}$) and the constant (E^{o}) in the Nicolsky equation by user-specified increments, and calculates the sum of the squares of the difference between calculated and measured potentials. The results are shown in Table 15.

As mentioned earlier, it is assumed in the graphical cross-point method that the electrode is responding only to one ion at the extreme ends of the concentration range.

TABLE 13
ACTIVITIES AND CORRECTED POTENTIALS FOR ELECTRODES G1 AND G2
IN $CaCl_2/BaCl_2$ MIXTURES

		ELECTRODE G1			ELECTRODE G2		
Ca Activity	Ba Activity	EMF-1	EMF-2	EMF-3	EMF-1	EMF-2	EMF-3
8.41×10^{-5}M	9.24×10^{-6}M	54.6mV	58.4mV	56.1mV	42.8mV	46.2mV	45.5mV
8.14×10^{-5}	9.69×10^{-5}	55.3	59.1	56.8	44.5	47.3	47.1
7.95×10^{-5}	1.80×10^{-4}	55.6	59.5	57.3	45.1	48.0	47.7
7.80×10^{-5}	2.60×10^{-4}	56.7	60.0	57.8	45.8	48.8	48.4
7.66×10^{-5}	3.39×10^{-4}	56.4	60.4	58.3	46.3	49.2	49.0
7.23×10^{-5}	6.09×10^{-4}	58.5	62.3	60.0	49.0	51.8	51.5
6.82×10^{-5}	9.85×10^{-4}	60.8	64.4	62.1	51.7	54.2	54.0
6.42×10^{-5}	1.44×10^{-3}	62.9	66.3	64.1	54.5	56.8	56.5
6.11×10^{-5}	1.85×10^{-3}	64.7	67.8	65.5	56.3	58.7	58.2
5.83×10^{-5}	2.24×10^{-3}	66.0	69.2	66.7	58.0	60.3	59.9
5.50×10^{-3}	2.76×10^{-3}	67.9	70.7	68.2	60.1	62.1	61.6
5.14×10^{-5}	3.61×10^{-3}	70.1	72.7	69.9	62.9	64.6	64.1
4.90×10^{-5}	4.39×10^{-3}	71.6	74.3	71.3	64.7	66.4	65.8
4.67×10^{-5}	5.09×10^{-3}	72.6	75.6	72.6	65.7	68.2	67.5
4.32×10^{-5}	6.38×10^{-3}	73.2	77.6	74.6	66.6	70.6	69.8
3.92×10^{-5}	8.12×10^{-3}	73.9	79.9	76.7	67.3	73.4	72.7
3.49×10^{-5}	1.05×10^{-2}	78.0	82.9	79.5	72.0	76.8	75.9
3.17×10^{-5}	1.26×10^{-2}	80.9	85.0	81.4	75.5	79.5	78.5
2.95×10^{-5}	1.45×10^{-2}	83.3	86.8	83.2	78.1	81.6	80.5
2.78×10^{-5}	1.62×10^{-2}	85.0	88.3	84.6	80.3	83.5	82.4

TABLE 13 - Continued

Ca Activity	Ba Activity	ELECTRODE G1			ELECTRODE G2		
		EMF-1	EMF-2	EMF-3	EMF-1	EMF-2	EMF-3
7.24×10^{-4}M	7.96×10^{-6}M	77.2mV	79.0mV	74.8mV	67.4mV	70.0mV	69.8mV
7.18×10^{-4}	8.53×10^{-5}	77.5	79.2	74.7	68.0	69.8	70.1
7.09×10^{-4}	1.61×10^{-4}	77.4	79.2	74.6	67.6	69.9	69.9
7.03×10^{-4}	2.34×10^{-4}	77.4	79.1	74.5	67.9	69.8	69.9
6.94×10^{-4}	3.07×10^{-4}	77.4	79.1	74.5	68.4	70.0	70.0
6.70×10^{-4}	5.64×10^{-4}	77.2	79.2	74.0	68.6	70.3	70.3
6.41×10^{-4}	9.23×10^{-4}	77.8	79.5	74.3	69.0	70.6	70.5
6.11×10^{-4}	1.36×10^{-3}	----	79.7	74.6	69.5	71.1	71.0
5.86×10^{-4}	1.77×10^{-3}	78.5	79.9	74.7	70.1	71.3	71.2
5.63×10^{-4}	2.14×10^{-3}	79.1	80.1	75.0	70.4	71.8	71.7
5.34×10^{-4}	2.66×10^{-3}	79.3	80.4	75.3	71.1	72.2	72.1
5.05×10^{-4}	3.49×10^{-3}	80.5	81.1	75.8	72.4	73.3	73.1
4.77×10^{-4}	4.23×10^{-3}	81.1	81.7	76.4	73.4	74.0	73.8
4.56×10^{-4}	4.94×10^{-3}	82.0	82.3	76.8	74.3	74.9	74.7
4.23×10^{-4}	6.21×10^{-3}	83.0	83.3	77.6	76.0	76.2	75.8
3.86×10^{-4}	7.91×10^{-3}	84.6	84.5	78.8	77.9	78.1	77.6
3.45×10^{-4}	1.03×10^{-2}	86.7	86.2	80.6	80.4	80.3	79.9
3.17×10^{-4}	1.24×10^{-2}	88.5	87.6	81.7	82.7	82.3	82.0
2.95×10^{-4}	1.43×10^{-2}	89.9	88.9	83.1	84.3	83.8	83.6
2.77×10^{-4}	1.61×10^{-2}	91.3	90.1	84.3	85.9	85.5	85.3

TABLE 13 - Continued

Ba Activity	Ca Activity	ELECTRODE G1			ELECTRODE G2		
		EMF-4	EMF-5	EMF-6	EMF-4	EMF-5	EMF-6
7.24×10^{-4}M	7.98×10^{-6}M	67.9mV	59.5mV	47.9mV	50.8mV	48.0mV	44.0mV
7.17×10^{-4}	8.56×10^{-5}	73.2	66.1	53.4	55.9	53.7	49.7
7.08×10^{-4}	1.62×10^{-4}	76.9	69.9	56.5	59.6	57.5	52.9
7.00×10^{-4}	2.36×10^{-4}	78.9	72.8	59.7	61.8	60.2	56.1
6.93×10^{-4}	3.09×10^{-4}	81.0	75.2	61.6	63.9	62.5	58.2
6.68×10^{-4}	5.65×10^{-4}	86.3	81.0	67.8	69.4	68.2	64.4
6.40×10^{-4}	9.28×10^{-4}	91.4	86.1	72.8	74.3	73.1	69.6
6.07×10^{-4}	1.37×10^{-4}	95.4	90.2	77.1	78.4	77.4	74.0
5.81×10^{-4}	1.79×10^{-3}	98.4	93.1	80.1	82.0	80.1	76.8
5.59×10^{-4}	2.17×10^{-3}	100.4	95.1	82.2	83.9	82.3	79.0
5.29×10^{-4}	2.70×10^{-3}	103.0	97.8	84.8	87.9	85.1	81.5
4.98×10^{-4}	3.55×10^{-3}	106.9	100.9	87.9	90.7	88.1	84.9
4.72×10^{-4}	4.33×10^{-3}	109.2	103.2	90.3	92.8	90.3	87.1
4.48×10^{-4}	5.07×10^{-3}	110.7	104.8	92.1	94.5	92.1	89.1
4.14×10^{-4}	6.38×10^{-3}	113.6	107.7	95.2	97.4	94.8	92.0
3.76×10^{-4}	8.23×10^{-3}	116.4	110.5	98.2	100.3	98.0	95.3
3.33×10^{-4}	1.07×10^{-2}	120.0	113.9	102.0	104.7	101.3	98.9
3.03×10^{-4}	1.30×10^{-2}	122.9	116.0	104.9	107.1	104.2	101.8
2.80×10^{-4}	1.50×10^{-2}	124.8	118.1	107.1	109.2	106.0	103.9
2.63×10^{-4}	1.69×10^{-2}	126.3	119.5	108.6	110.7	107.9	105.5

TABLE 13 - Continued

		ELECTRODE G1		ELECTRODE G2	
Ba Activity	Ca Activity	EMF-5	EMF-6	EMF-5	EMF-6
3.73×10^{-3}M	5.92×10^{-6}M	70.6mV	60.7mV	64.2mV	59.9mV
3.71×10^{-3}	6.39×10^{-5}	72.2	61.8	65.9	61.5
3.69×10^{-3}	1.21×10^{-4}	73.6	63.2	67.0	62.6
3.68×10^{-3}	1.78×10^{-4}	74.8	64.2	68.1	63.8
3.66×10^{-3}	2.35×10^{-4}	75.8	65.2	69.1	64.7
3.60×10^{-3}	4.39×10^{-4}	79.2	68.8	72.3	68.2
3.54×10^{-3}	7.36×10^{-4}	82.8	72.6	75.7	71.7
3.43×10^{-3}	1.11×10^{-3}	86.1	76.0	79.0	75.1
3.34×10^{-3}	1.48×10^{-3}	88.6	78.5	81.4	77.5
3.26×10^{-3}	1.82×10^{-3}	90.5	80.5	83.4	79.5
3.14×10^{-3}	2.30×10^{-3}	92.9	82.8	85.7	81.8
3.01×10^{-3}	3.09×10^{-3}	95.9	85.9	88.8	85.1
2.89×10^{-3}	3.83×10^{-3}	98.2	88.4	91.0	87.4
2.80×10^{-3}	4.54×10^{-3}	100.0	90.3	92.9	89.4
2.64×10^{-3}	5.84×10^{-3}	102.9	93.2	95.6	92.1
2.45×10^{-3}	7.62×10^{-3}	106.0	96.4	98.8	95.6
2.20×10^{-3}	1.02×10^{-2}	109.7	100.4	102.5	99.5
2.04×10^{-3}	1.25×10^{-2}	112.3	103.0	105.2	102.3
1.90×10^{-3}	1.46×10^{-2}	114.4	105.1	107.1	104.3
1.78×10^{-3}	1.66×10^{-2}	116.1	106.8	109.0	106.1

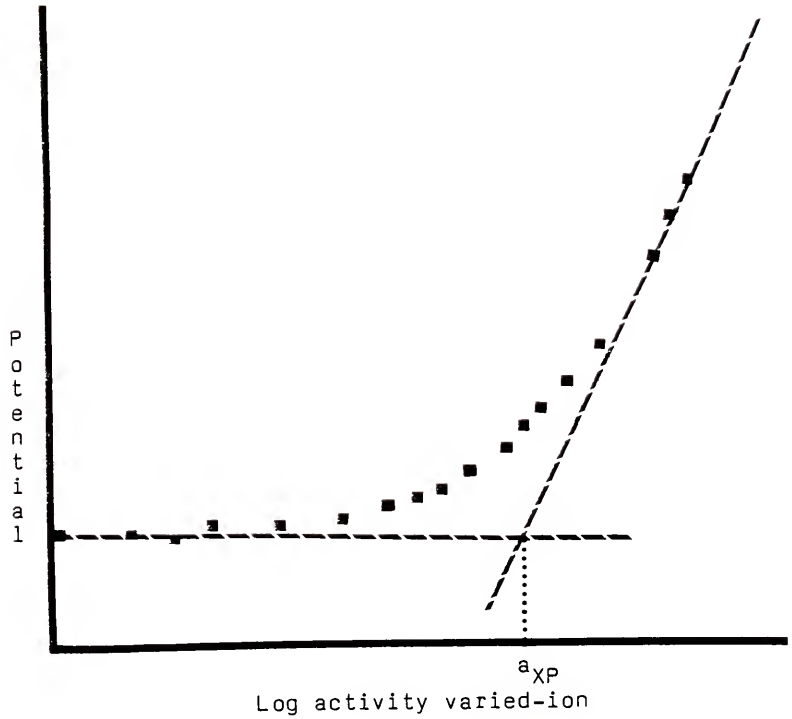

FIGURE 8. Determination of the Varied-ion Concentration at the Cross-point.

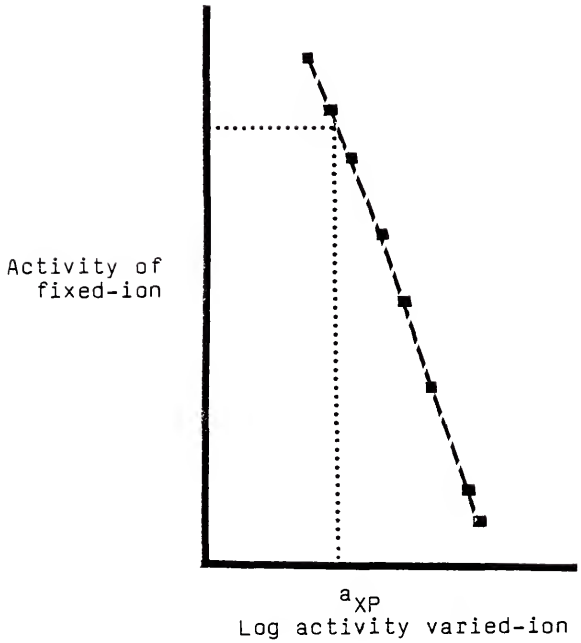

FIGURE 9. Determination of the Fixed-ion Concentration at the Cross-point.

TABLE 14

MIXED SOLUTION CROSS-POINT SELECTIVITY COEFFICIENTS $k^{XP}_{Ca,Ba}$ AND $k^{XPR}_{Ca,Ba}$ FOR ELECTRODES G1 AND G2

Electrode G1

Concentration	XP-1 $k^{XP}_{Ca,Ba}$	XP-2 $k^{XP}_{Ca,Ba}$	XP-3 $k^{XP}_{Ca,Ba}$	XPR-1 $k^{XPR}_{Ca,Ba}$	XPR-2 $k^{XPR}_{Ca,Ba}$
4.55×10^{-4} M $CaCl_2$	.0890	.0798	.0708	.0220	.0260
6.37×10^{-4}	.0629	.0760	.0851	.0176	.0262
9.10×10^{-4}	.122	.109	.0952	.0322	.0375
2.73×10^{-3}	.163	.150	.159	.0496	.0576
4.55×10^{-3}	---	.198	.228	---	.0796
Standard Deviation	.043	.052	.065	.0142	.0231
Relative Std. Dev.	40%	42%	51%	47%	51%
	XP-4 $k^{XP}_{Ca,Ba}$	XP-5 $k^{XP}_{Ca,Ba}$	XP-6 $k^{XP}_{Ca,Ba}$	XPR-4 $k^{XPR}_{Ca,Ba}$	XPR-5 $k^{XPR}_{Ca,Ba}$
2.73×10^{-3} M $BaCl_2$	.190	.122	.187	.103	.0720
4.55×10^{-3}	.125	.131	.124	.0796	.0800
6.37×10^{-3}	---	.110	.106	---	.0688
Standard Deviation	.046	.015	.043	0.023	.0058
Relative Std. Dev.	29%	8.7%	31%	26%	7.8%

Electrode G2

XP-3 $k_{Ca,Ba}$	XP-1 $k_{Ca,Ba}$	XP-2 $k_{Ca,Ba}$	XP-3 $k_{Ca,Ba}$	XP-4 $k_{Ca,Ba}$	XP-5 $k_{Ca,Ba}$	XP-6 $k_{Ca,Ba}$
.0165	.0887	.0736	.0905	.0471	.0423	.0458
.0204	.0530	.0975	.0911	.0302	.0563	.0475
.0239	.136	.116	.116	.0737	.0679	.0611
.0445	.181	.193	.172	.105	.118	.0962
.0652	---	.228	.266	---	.142	.0149
.0205	.056	.066	.074	.0327	.0427	.0436
60%	49%	46%	50%	51.1%	50%	54.6%

XPR-6 $k_{Ca,Ba}$	XP-4 $k_{Ca,Ba}$	XP-5 $k_{Ca,Ba}$	XP-6 $k_{Ca,Ba}$	XPR-4 $k_{Ca,Ba}$	XPR-5 $k_{Ca,Ba}$	XPR-6 $k_{Ca,Ba}$
.0849	.181	.173	.182	0.123	.0635	.0522
.0594	.138	.142	.167	.0966	.0557	.0519
.0525	---	.101	.105	---	.0413	.0345
.0171	.030	.036	.041	0.019	.0113	.0101
26%	19%	26%	27%	17%	21.1%	21.9%

TABLE 15
CURVE-FITTING SELECTIVITY COEFFICIENTS FOR ELECTRODES G1 AND G2

Electrode G1

Concentration[a]		DAY 1	DAY 2	DAY 3	DAY 4	DAY 5	DAY 6
9.10×10^{-5}M Ca					9.10×10^{-4}M Ba		
	E^0	153.0	145.1	140.8	175.8	167.0	160.4
	S	24.14	21.46	20.89	28.33	27.06	29.43
	K	.0805	.111	.105	.200	.140	.180
	r	16.2	10.1	5.2	3.1	0.7	7.1
2.73×10^{-4}M Ca					2.73×10^{-3}M Ba		
	E^0	154.6	147.9	140.2	171.3	158.5	162.0
	S	24.83	22.27	20.92	29.28	24.42	30.98
	K	.0900	.116	.120	.180	.120	.200
	r	6.9	3.8	5.0	4.4	35.8	4.1
4.55×10^{-4}M Ca					4.55×10^{-3}M Ba		
	E^0	157.4	157.8	146.5	171.0	167.5	163.8
	S	25.90	24.79	22.52	29.37	29.35	31.58
	K	.137	.0959	.102	.160	.150	.160
	r	4.2	0.8	1.2	3.7	3.1	5.7
6.37×10^{-4}M Ca					6.37×10^{-3}M Ba		
	E^0	156.3	149.0	140.9		166.8	163.5
	S	24.98	22.28	20.95		29.22	31.78
	K	.120	.120	.100		.160	.160
	r	10.0	1.1	1.4		15.9	4.1
9.10×10^{-4}M Ca					9.10×10^{-3}M Ba		
	E^0	156.6	148.9	140.7		177.7	168.0
	S	25.12	22.32	21.10		29.50	32.09
	K	.120	.120	.100		0.130	0.142
	r	5.6	0.8	2.1		9.9	2.0
2.73×10^{-3}M Ca							
	E^0	156.9	149.6	141.0			
	S	24.60	21.77	20.71			
	K	.140	.120	.120			
	r	0.3	0.9	1.7			
4.55×10^{-3}M Ca							
	E^0		150.1	146.1			
	S		21.49	20.73			
	K		.120	.140			
	r		0.4	4.9			

[a] E^0 is the standard potential for the electrode in mV, S is the response slope in mV, K is the selectivity coefficient obtained by curve fitting, and r is the correlation coefficient for the curve-fitting.

TABLE 15 - Continued

Electrode G2

Concentration[a]	DAY 1	DAY 2	DAY 3	DAY 4	DAY 5	DAY 6
9.10×10^{-5}M Ca				9.10×10^{-4}M Ba		
E^0	146.5	147.8	155.1	161.4	157.4	152.8
S	25.48	25.13	26.93	29.18	28.46	27.90
K	.126	.133	.107	.230	.199	.165
r	11.8	18.7	5.9	6.3	3.0	12.8
2.73×10^{-4}M Ca				2.73×10^{-3}M Ba		
E^0	152.7	148.3	156.7	160.2	157.4	156.7
S	27.08	25.40	27.46	28.85	28.20	29.72
K	.125	.145	.108	.160	.160	.180
r	9.0	9.7	5.0	1.8	4.4	5.7
4.55×10^{-4}M Ca				4.55×10^{-3}M Ba		
E^0	145.7	148.9	147.7	160.1	156.8	159.8
S	25.01	25.11	24.74	29.01	27.97	30.66
K	.160	.130	.121	.160	.140	.150
r	14.5	12.1	14.8	2.6	4.5	1.4
6.37×10^{-4}M Ca				6.37×10^{-3}M Ca		
E^0	148.3	149.8	148.3		160.6	159.2
S	25.68	25.50	24.95		29.28	30.45
K	.181	.140	.141		.139	.159
r	97.6	4.8	3.9		1.0	6.1
9.10×10^{-4}M Ca				9.10×10^{-3}M Ca		
E^0	152.6	149.5	147.1		161.4	157.0
S	26.70	25.29	24.56		29.58	28.21
K	.140	.140	.140		.139	.0901
r	23.4	5.6	6.9		1.0	8.3
2.73×10^{-3}M Ca						
E^0	153.7	149.1	147.0			
S	27.02	25.21	24.34			
K	.180	.180	.180			
r	0.9	1.5	1.7			
4.55×10^{-3}M Ca						
E^0		149.6	152.1			
S		24.93	25.65			
K		.140	.155			
r		5.9	2.2			

a E^0 is the standard potential for the electrode in mV, S is the response slope in mV, K is the selectivity coefficient obtained by curve fitting, and r is the correlation coefficient for the curve-fitting.

This means that the potential of the electrode at the lowest activity of the varied-ion should be the same as that observed for the other (fixed activity) ion in pure solution, and that the potentials observed at the highest activities of the varied-ion should display the same slope as is observed in pure solutions of that ion. The slopes of the linear portion obtained at the high activity end for the twelve fixed-ion concentrations have been calculated; they are shown in Table 16 along with the separate solution calibration slopes. The potentials at the lower varied-ion concentrations were considered as a function of the fixed-ion concentration, and a slope and y-intercept calculated. These results are compared in Table 17 to the separate solution values.

The mixed solution measurements were also used as a check on the ability of the selectivity coefficients measured in separate solution to describe the response of the electrode in mixed solutions. For this purpose a selectivity coefficient was calculated from Eqn. 38 using the slopes and y-intercepts calculated from separate solution measurements. This selectivity coefficient was then used to calculate the potential according to the modified Nicolsky equation:

$$E = E_A^o + S_A \log \left(a_A + k_{A,B}^R \, a_B^{S_B/S_A}\right) \qquad (49)$$

A representative sample of these results is given in Table 18.

TABLE 16
COMPARISON OF SEPARATE SOLUTION AND HIGH ACTIVITY MIXED SOLUTION RESPONSE SLOPES FOR ELECTRODES G1 AND G2

Electrode G1

Concentration	DAY 1	DAY 2	DAY 3	DAY 4	DAY 5	DAY 6
Ca Calibration				26.8;161.1[a]	26.3;156.6	27.1;155.5
Ba Calibration	24.6;129.8	22.1;126.6	20.7;120.8			
4.55×10^{-4}M Ca	28.9;142.0	24.9;134.2	23.1;124.6			
6.37×10^{-4}M Ca	35.1;154.7	22.4;130.0	21.3;122.4			
9.10×10^{-4}M Ca	23.6;133.5	20.1;126.1	19.3;118.7			
2.73×10^{-3}M Ca	16.2;124.3	16.2;123.7	15.2;115.8			
4.55×10^{-3}M Ca		10.0;114.7	12.6;119.2			
9.10×10^{-3}M Ca				28.3;175.7	27.7;168.5	30.2;161.3
2.73×10^{-3}M Ca				28.9;171.5	27.8;164.7	29.2;158.3
4.55×10^{-3}M Ca				27.2;166.7	27.1;162.9	28.2;156.8
6.37×10^{-3}M Ca					25.8;160.6	26.7;152.9
Average slope	26.0	18.7	18.3	28.1	27.1	28.6
Std.Deviation	8.0	5.8	4.3	0.86	0.9	1.5

TABLE 16 - Continued

Electrode G2

Concentration	DAY 1	DAY 2	DAY 3	DAY 4	DAY 5	DAY 6
Ca Calibration				26.4;150.1	27.0;152.4	27.3;151.3
Ba Calibration	26.9;127.3	24.9;124.8	24.1;121.7			
4.55×10^{-4}M Ca	36.4;150.4	31.6;141.2	30.0;137.5			
6.37×10^{-4}M Ca	63.6;204.8	27.8;134.5	29.1;136.8			
9.10×10^{-4}M Ca	28.2;136.4	26.5;132.9	27.6;134.7			
2.73×10^{-4}M Ca	21.6;127.3	21.4;126.9	23.1;130.1			
4.55×10^{-3}M Ca		16.2;119.3	15.2;118.4			
9.10×10^{-3}M Ca				29.8;163.0	28.0;156.4	29.9;157.7
2.73×10^{-3}M Ca				28.2;159.0	27.2;156.7	29.4;156.6
4.55×10^{-3}M Ca				26.9;155.9	26.9;155.0	28.9;156.2
6.37×10^{-3}M Ca					25.5;152.7	26.6;151.8
Average Slope	28.7	24.7	25.0	28.2	27.2	28.7
Std.Deviation	7.4	6.0	6.1	1.2	1.0	1.5

[a] the first value in each pair is the response slope in mV/1 decade; the second value is the y-intercept (E_o) in mV.

TABLE 17
COMPARISON OF SEPARATE SOLUTION AND LOW ACTIVITY MIXED SOLUTION RESPONSE SLOPES FOR ELECTRODES G1 AND G2

Concentration	DAY 1	DAY 2	DAY3	DAY 4	DAY 5	DAY 6
Electrode G1						
Ca Calibration	32.4;174.1[a]	27.5;161.8	28.0;161.4			
Ba Calibration				24.2;123.8	24.1;122.1	23.7;119.8
Ca ion fixed	26.0;159.6	24.3;156.4	23.2;149.2			
Ba ion fixed				6.0;86.3	21.7;126.9	21.1;113.3
Electrode G2						
Ca Calibration	30.2;160.4	27.6;154.4	27.3;153.1			
Ba Calibration				24.8;122.5	22.7;115.6	21.9;110.7
Ca ion fixed	27.6;154.5	25.8;150.7	26.6;153.7			
Ba ion fixed				19.0;110.3	23.2;120.5	22.7;114.9

[a] The first value in each pair is the response slope in mV/decade; the second value is the y-intercept (E^0) in mV.

TABLE 18
COMPARISON OF CALCULATED AND MEASURED POTENTIALS
FOR ELECTRODES G1 AND G2

	E-measured	E-calculated	Error
Electrode G1, Day 1	69.7 mV	63.7 mV	6.0 mV
4.55×10^{-4}M $CaCl_2$	69.6	64.6	5.0
	69.6	65.2	4.4
	69.7	65.6	4.1
	69.8	66.0	3.8
	70.4	67.1	3.3
	71.0	68.5	2.5
	71.8	69.9	1.9
	72.7	71.0	1.7
	73.4	71.9	1.5
	74.3	74.6	1.1
	75.7	73.0	1.3
	77.0	75.9	1.1
	78.1	76.9	1.2
	80.2	78.6	1.6
	82.1	80.5	1.6
	84.7	82.7	2.0
	87.3	84.4	2.9
	88.8	85.7	3.1
	90.3	86.8	3.5
Electrode G2, Day 1	60.0mV	57.4mV	2.6mV
4.55×10^{-4}M $CaCl_2$	60.3	57.8	2.5
	60.5	58.1	2.4
	60.8	58.4	2.4
	60.8	58.6	2.2
	61.6	59.4	2.2
	62.3	60.6	1.7
	63.5	61.8	1.7
	64.4	62.9	1.5
	65.4	63.8	1.6
	66.3	64.9	1.4
	68.3	66.6	1.7
	69.8	68.0	1.8
	71.1	69.1	2.0
	72.9	70.9	2.0
	75.5	73.0	2.5
	78.2	75.5	2.7
	80.7	77.4	3.3
	84.4	78.9	5.5
	84.6	80.0	4.6

TABLE 18 - Continued

	E-measured	E-calculated	Error
Electrode G1, Day 6 4.55×10^{-3}M $BaCl_2$	58.2mV	59.7mV	-1.5mV
	60.5	62.0	-1.5
	61.9	63.8	-1.9
	63.3	65.4	-2.1
	64.4	66.8	-2.4
	68.5	70.8	-2.3
	72.6	74.8	-2.2
	76.3	78.4	-2.1
	79.0	81.2	-2.2
	81.0	83.2	-2.2
	83.7	86.7	-2.0
	86.8	88.8	-2.0
	89.1	91.0	-1.9
	90.0	92.9	-2.0
	93.9	95.7	-1.8
	97.2	98.6	-1.4
	100.8	102.0	-1.2
	103.5	104.2	-0.7
	105.5	105.9	-0.4
	107.1	107.3	-0.2
Electrode G2, Day 6 4.55×10^{-3}M $BaCl_2$	56.5mV	55.2mV	1.3mV
	58.7	57.4	1.3
	60.0	59.2	0.8
	61.4	60.8	0.6
	62.5	62.2	0.3
	66.5	66.1	0.4
	70.4	70.1	0.3
	74.1	73.8	0.3
	76.7	76.5	0.2
	78.9	78.5	0.4
	81.4	81.0	0.4
	84.7	84.1	0.6
	86.9	86.4	0.5
	88.9	88.3	0.6
	91.9	91.0	1.3
	95.3	94.0	1.3
	98.9	97.4	1.5
	101.8	99.6	2.2
	103.9	101.3	2.6
	105.8	102.8	3.1

Neutral Carrier Electrode based on AC-14/81

Experimental System

The experimental apparatus has already been described. The calcium ion activity was fixed at one of four levels--2×10^{-3}, 3×10^{-3}, 4×10^{-3} and 8×10^{-3}--and the sodium ion concentration was varied from 9×10^{-5} M to 2×10^{-5} M.

Data Treatment

Activity coefficients and diffusion potentials were calculated as before; activities and corrected potentials are shown in Table 19 and in Appendix B.

It was not possible to use the graphical cross-point approach, since a horizontal initial line was not observed for any of the fixed-ion concentrations.

A comparison of the slopes of the linear portion at the high activity end and the separate solution calibration slopes was made; the results are shown in Table 20.

Expected potentials were again calculated according to the modified Nicolsky equation using the separate solution selectivity coefficient given by Eqn. 38. A representative sample of the results is given in Table 21.

Ion-Exchange Electrode for Calcium Ion

Experimental System

The experimental apparatus has already been described. Since the response of the electrode was rather slow it was only possible to obtain data for one fixed concentration on each of five days. The fixed concentration was 4.903×10^{-3}

TABLE 19
ACTIVITIES AND CORRECTED POTENTIALS FOR ELECTRODES Q1 AND Q2 IN $NaCl/CaCl_2$ MIXTURES

Activity Na	Activity Ca	EMF-1	EMF-2	EMF-3	EMF-4	EMF-5
Electrode Q1						
8.56×10^{-5}M	1.89×10^{-3} M	-----	-41.3mV	-37.4mV	-39.4mV	-40.5mV
1.71×10^{-4}	1.88×10^{-3}	-----	-38.0	-34.4	-36.2	-37.1
3.41×10^{-4}	1.87×10^{-3}	-----	-32.5	-29.6	-31.0	-32.4
5.94×10^{-4}	1.86×10^{-3}	-----	-25.1	-22.9	-24.2	-25.1
9.28×10^{-4}	1.84×10^{-3}	-----	-18.3	-16.4	-17.6	-18.3
1.26×10^{-3}	1.82×10^{-3}	-----	-12.5	-11.1	-12.1	-12.7
1.59×10^{-3}	1.80×10^{-3}	-----	- 8.3	- 6.8	- 7.5	- 8.5
2.07×10^{-3}	1.77×10^{-3}	-----	- 2.8	- 1.2	- 2.2	- 3.0
2.93×10^{-3}	1.74×10^{-3}	-----	3.5	5.4	4.5	3.5
4.61×10^{-3}	1.69×10^{-3}	-----	13.3	15.4	-----	13.6
6.27×10^{-3}	1.65×10^{-3}	-----	19.5	21.8	20.8	19.2
8.72×10^{-3}	1.58×10^{-3}	-----	27.0	29.7	28.0	27.0
1.27×10^{-2}	1.50×10^{-3}	-----	34.5	37.5	36.6	34.5
2.03×10^{-2}	1.37×10^{-2}	-----	45.5	48.8	47.0	45.5
Electrode Q2						
8.56×10^{-5}M	1.89×10^{-3} M	-----	-32.5mV	-23.6mV	-27.4mV	-26.5mV
1.71×10^{-4}	1.88×10^{-3}	-----	-30.1	-21.4	-25.2	-23.9
3.41×10^{-4}	1.87×10^{-3}	-----	-24.7	-16.4	-19.7	-18.7
5.94×10^{-4}	1.86×10^{-3}	-----	-18.0	-10.0	-13.4	-12.7
9.28×10^{-4}	1.84×10^{-3}	-----	-11.5	- 3.6	- 6.9	- 6.4
1.26×10^{-3}	1.82×10^{-3}	-----	- 7.1	2.1	- 1.7	- 1.5
1.59×10^{-3}	1.80×10^{-3}	-----	- 2.8	6.4	2.5	2.6
2.07×10^{-3}	1.77×10^{-3}	-----	1.5	11.1	7.6	7.6
2.93×10^{-3}	1.74×10^{-3}	-----	8.0	17.6	14.4	14.1
4.61×10^{-3}	1.69×10^{-3}	-----	16.8	26.5	-----	23.4
6.27×10^{-3}	1.65×10^{-3}	-----	23.3	32.9	30.0	28.1
8.72×10^{-3}	1.58×10^{-3}	-----	30.2	35.9	37.3	34.2
1.27×10^{-2}	1.50×10^{-3}	-----	38.3	43.6	45.2	42.5
2.03×10^{-2}	1.37×10^{-2}	-----	47.6	53.2	55.7	51.3

EMF-6	EMF-7	EMF-8	EMF-9	EMF-10	EMF-11	EMF-12
-41.7mV	-41.0mV	-43.3mV	-47.8mV	-50.4mV	-48.2mV	-50.8mV
-38.5	-37.9	-40.5	-44.3	-46.9	-44.8	-47.1
-33.2	-32.6	-35.3	-38.3	-41.0	-39.2	-40.8
-26.1	-26.9	-28.6	-31.0	-33.4	-31.7	-32.9
-19.1	-20.5	-21.5	-23.2	-25.6	-24.4	-25.3
-13.5	-15.2	-16.0	-17.7	-20.0	-18.7	-19.4
- 9.2	-10.7	-11.4	-13.1	-15.2	-14.2	-14.7
- 3.6	- 5.4	- 6.0	- 7.6	- 9.8	- 8.4	- 9.1
3.2	1.4	0.9	- 0.5	- 2.8	- 2.1	- 1.8
12.9	11.3	10.5	9.6	7.3	8.6	8.1
19.6	18.0	17.2	16.4	14.6	15.2	15.1
27.0	25.4	24.7	24.0	23.1	22.9	22.6
35.4	34.0	33.3	32.6	32.1	31.0	31.2
46.4	44.9	44.2	43.5	42.9	42.6	42.1

-28.8mV	-29.1mV	-28.4mV	-32.4mV	-34.0mV	-34.4mV
-26.2	-26.8	-26.3	-29.3	-31.4	-31.1
-20.8	-22.0	-21.2	-24.0	-26.5	-26.7
-14.2	-16.3	-15.1	-17.5	-20.6	-19.8
- 7.6	-10.1	- 8.7	-11.0	-13.5	-14.3
- 2.2	- 5.0	- 3.8	- 5.7	- 8.2	- 8.1
2.0	- 0.9	0.4	- 1.3	- 3.8	- 4.9
7.4	4.0	5.5	4.4	0.5	0.3
14.1	10.6	12.3	10.8	7.6	6.0
23.0	20.3	21.5	20.2	17.6	16.5
29.5	26.8	28.2	26.9	24.6	22.7
36.0	33.9	35.4	34.5	32.4	30.2
44.4	42.4	43.7	43.0	41.2	37.8
52.2	53.1	53.5	53.7	51.9	47.2

TABLE 20
COMPARISON OF SEPARATE SOLUTION AND HIGH ACTIVITY MIXED SOLUTION RESPONSE SLOPES FOR ELECTRODES Q1 AND Q2

Electrode Q1	DAY 1	DAY 2	DAY 3	DAY 4	DAY 5	DAY 6
Ca Calibration	20.8;9.5[a]	20.2;6.9	20.5;13.2	19.7;9.3	19.9;7.5	20.4;9.1
Na Calibration	47.9;127.6	45.5;118.8	49.1;130.2	48.3;127.0	48.3;126.6	46.9;122.7
2.73×10^{-3}M Ca		50.0;129.8	51.9;136.4	51.5;134.2	49.8;129.4	52.1;134.4
4.54×10^{-3}M Ca	52.5;137.5	51.6;132.9	51.5;134.2	51.3;134.8	48.8;125.0	51.1;131.0
6.34×10^{-3}M Ca	52.0;137.1	51.9;135.0	53.5;139.3	51.6;134.7	52.0;133.5	51.7;131.7
1.79×10^{-2}M Ca	49.5;132.8	49.3;130.8	50.9;133.3	49.7;132.5	50.2;133.0	50.1;129.6
Electrode Q2						
Ca Calibration	21.8;19.3	20.7;16.4	20.0;21.7	19.9;18.8	20.6;119.7	20.4;21.3
Na Calibration	48.2;130.4	47.1;125.4	47.8;136.3	45.7;127.3	48.1;131.2	48.2;132.0
2.73×10^{-3}M Ca		48.1;129.2	40.5;121.0	50.2;140.7	49.3;126.3	45.9;130.5
4.54×10^{-3}M Ca	51.6;139.4	48.8;130.8	52.7;145.8	49.7;144.1	50.1;138.5	47.1;133.2
6.34×10^{-3}M Ca	48.0;131.9	51.2;138.2	49.0;137.1	--------	50.5;139.3	
1.79×10^{-2}M Ca	48.0;132.6	48.3;132.5	46.8;130.8	48.9;136.8	49.3;139.1	49.2;136.8

[a] The first value in each pair is the response slope in mV/decade; the second value is the y-intercept (E^o) in mV.

TABLE 20 - Continued

Electrode G1	DAY 7	DAY 8	DAY 9	DAY 10	DAY 11	DAY 12
Ca Calibration	20.4;9.5	19.9;4.2	19.9;1.4	17.1;-9.7	20.4;0.5	17.3;-13.1
Na Calibration	45.5;116.6	48.8;125.6	48.9;124.6	48.1;123.4	46.3;115.2	49.6;124.4
2.73×10^{-3}M Ca	52.3;133.3	52.5;133.0	52.8;132.8	55.6;137.4	52.7;131.5	52.8;131.5
4.54×10^{-3}M Ca						
6.34×10^{-3}M Ca	52.1;132.8	52.2;132.8	51.6;130.9	53.6;133.8	53.3;133.6	53.0;132.7
1.79×10^{-3}M Ca	51.5;131.9	50.5;128.0	50.9;130.4	51.4;130.1	52.3;132.4	51.4;131.1
Ca Calibration	21.3;23.2	20.7;21.7	21.6;22.0	18.8;10.1	21.6;18.7	
Na Calibration	46.9;127.0	50.1;138.5	50.0;136.8	49.2;135.1	48.5;124.0	
2.73×10^{-3}M Ca	51.1;139.4	49.9;138.1	52.2;142.1	53.5;142.6	48.0;128.7	
4.54×10^{-3}M Ca						
6.34×10^{-3}M Ca	50.3;137.7	49.8;138.7	53.0;144.5	51.6;138.3	45.5;124.7	
1.79×10^{-2}M Ca	48.7;134.1	47.0;131.1	49.4;137.2	49.6;135.4	48.0;131.5	

TABLE 21
COMPARISON OF CALCULATED AND MEASURED POTENTIALS
FOR ELECTRODES Q1 AND Q2

6.3×10^{-3}M Ca Oay 1			6.3×10^{-3}MCa Oay 6			6.3×10^{-3}MCa Oay 11		
E-meas	E-calc	Error	E-meas	E-calc	Error	E-meas	E-calc	Error
-35.0	-36.0	1.0	-40.4	-35.9	-4.5	-41.4	-43.9	2.5
-32.6	-32.0	0.6	-37.7	-32.3	-5.4	-38.9	-39.9	1.0
-28.2	-25.8	-2.4	-32.7	-26.5	-6.2	-34.8	-33.7	-1.1
-22.3	-19.0	-3.3	-27.0	-20.1	-6.9	-28.9	-26.9	-2.0
-16.5	-12.5	-4.0	-20.5	-14.0	-6.5	-22.5	-20.5	-2.0
-11.2	- 7.5	-3.7	-15.3	- 9.2	-6.1	-17.4	-15.7	-1.7
- 6.8	- 3.7	-3.1	-10.9	- 5.5	-4.5	-12.5	-11.9	-0.6
- 1.7	- 1.0	-2.7	- 5.3	- 0.9	-4.4	- 7.5	- 7.2	-0.3
4.9	7.5	-2.6	1.0	5.3	-4.3	- 1.2	- 1.0	-0.2
14.4	16.3	-1.9	10.6	13.8	-3.2	8.5	7.5	1.0
21.8	22.4	-0.6	17.0	19.7	-2.7	15.5	13.4	2.1
29.2	29.0	0.2	24.6	26.2	-1.6	23.0	19.8	3.2
38.0	36.6	1.4	32.5	33.6	-1.1	31.8	27.2	4.6
48.5	46.3	2.2	43.8	43.1	0.7	42.9	36.6	6.3
E-meas	E-calc	Error	E-meas	E-calc	Error	E-meas	E-calc	Error
-27.6	-29.6	2.0	-27.5	-24.8	-2.7	-28.5	-30.8	2.3
-25.9	-26.4	0.5	-24.9	-22.0	-2.9	-25.9	-28.3	2.4
-21.4	-21.0	-0.4	-20.6	-17.3	-3.3	-22.6	-24.1	1.5
-16.1	-15.0	-1.1	-15.0	-11.7	-3.3	-16.0	-19.0	3.0
-10.5	- 9.0	-1.5	- 9.3	- 6.2	-3.1	-11.7	-13.7	2.0
- 5.8	- 4.3	-0.7	- 4.0	- 1.7	-2.3	- 6.7	- 9.5	2.8
- 1.8	- 0.6	-1.2	- 0.1	1.8	-1.9	- 3.6	- 6.1	2.5
3.3	3.9	-0.6	4.4	6.2	-1.8	1.7	- 1.9	3.6
9.5	10.1	-0.6	10.8	12.2	-1.3	7.2	4.0	3.2
18.3	18.8	-0.5	20.1	20.7	-0.6	17.7	12.4	5.3
25.2	24.8	0.4	26.6	26.6	-0.0	23.3	18.2	5.1
32.2	31.4	0.8	32.9	33.1	-0.2	30.4	24.7	5.7
41.0	39.0	2.0	41.9	40.7	1.2	38.7	32.2	6.5
49.7	48.7	1.0	52.0	50.3	1.7	46.6	41.9	4.7

M barium chloride. The calcium chloride concentration was varied between 10^{-5} M and 10^{-2} M.

Data Treatment

Activity coefficients and diffusion potentials were again calculated; activities and corrected potentials are given in Table 22.

The measured potentials have again been compared to those calculated using a separate solution selectivity coefficient; these are shown in Table 23.

TABLE 22
ACTIVITIES AND CORRECTED POTENTIALS FOR THE CORNING ELECTRODE IN $CaCl_2/BaCl_2$ MIXTURES

Log Act Ca	Log Act Ba	EMF-1	EMF-2	EMF-3	EMF-4	EMF-5
-5.212	-2.516	40.4mV	37.4mV	37.1mV	34.1mV	39.8mV
-5.038	-2.519	39.1	36.4	35.6	34.7	37.3
-4.914	-2.520	39.5	36.4	36.5	30.7	38.1
-4.373	-2.523	45.3	44.3	44.9	40.7	45.2
-4.141	-2.526	51.9	52.5	51.6	47.8	50.9
-3.438	-2.536	74.4	73.9	73.8	71.4	70.9
-3.191	-2.545	82.1	81.5	81.7	80.2	79.7
-2.513	-2.609	102.9	102.4	102.1	100.9	100.6
-2.298	-2.654	109.9	108.9	-	-	107.2

TABLE 23
COMPARISON OF CALCULATED AND MEASURED POTENTIALS
FOR THE CORNING ELECTRODE

DAY 1			DAY 2			DAY 3			DAY 4			DAY 5		
E-meas	E-calc	Error	E-meas	E-calc	Error	E-meas	E-calc	Error	E-meas	E-calc	Error	E-meas	E-calc	Error
40.4mV	43.1mV	2.7mV	37.4mV	40.8mV	3.4mV	37.1mV	41.2mV	4.1mV	34.1mV	38.2mV	4.1mV	39.8mV	41.5mV	1.7mV
39.1	44.1	5.0	36.4	42.1	5.7	35.6	42.4	6.8	34.7	39.6	5.6	37.3	42.5	5.2
39.5	45.1	5.6	36.4	43.4	7.0	36.5	43.4	6.9	30.7	40.8	10.1	38.1	43.5	5.4
45.3	52.3	7.0	44.3	51.6	7.3	44.9	51.0	6.1	40.7	49.3	8.6	45.2	50.7	5.5
51.9	57.0	5.1	52.5	56.6	4.1	51.6	55.8	4.2	47.8	54.3	6.5	50.9	55.3	4.4
74.4	75.0	0.6	73.9	74.6	0.7	73.8	73.8	0.0	71.4	73.0	1.6	70.9	73.0	2.1
82.1	82.3	0.2	81.5	81.5	0.0	81.7	80.9	-0.8	80.2	80.1	-0.1	79.7	80.0	0.3
102.9	102.5	-0.4	102.4	101.0	-1.4	102.1	100.9	-1.2	100.9	100.3	-0.6	100.6	100.0	-0.6
109.9	109.0	-0.9	108.9	107.3	-1.6	-	-	-						

CHAPTER 7
DISCUSSION OF RESULTS

The interpretation of the results of these experiments is hindered somewhat by the lack of reproducibility of the measured data. Comparison of the potentials observed for a particular concentration over several days (Tables 3, 6, 7, 10, 13, 19, 22 and Appendices A and B) shows that the potential often changes as much as 4 mV. Despite this difficulty, however, several trends can be seen.

First, it is clear from the results shown in Tables 4, 5, 8, 9 and 11 for the separate solution method that the selectivity coefficient $k^{R}_{A,B}$ (calculated using measured slopes) is much less activity dependent than the Nicolsky selectivity coefficient $k^{pot}_{A,B}$. For example, the results for electrode G1 for day 1 of the measurements show a relative standard deviation of about 26% in $k^{pot}_{Ca,Ba}$ over the activity range, while the relative standard deviation for $k^{R}_{Ca,Ba}$ over the same activity range is only about 5%. For electrode Q1 on day 1 the improvement is less dramatic, with a relative standard deviation of about 6.4% for $k^{pot}_{Na,Ca}$ and 1.6% for $k^{R}_{Na,Ca}$. The largest improvement is seen with the Corning electrode, from a relative standard deviation of 100% for $k^{pot}_{Ca,Ba}$ to only 7% for $k^{R}_{Ca,Ba}$ on day 1. This variation in improvement among the three electrodes is easily explained

when one considers the degree to which they deviate from Nernstian behavior. Electrode Q1, which showed the least improvement, exhibited an average slope of 19.7 mV per decade for calcium and 47.8 mV for sodium over the twelve days on which measurements were made. This is a ratio of 2.4:1, not very different from the Nernstian prediction of 2:1 for a divalent/monovalent cation mixture. Electrode G1 exhibited an average slope of 28.0 mV for calcium and 23.2 mV for barium over the six days of use. This gives a ratio of 1.3:1 rather than the Nernstian 1:1, a somewhat larger deviation than that for Electrode Q1. The Corning electrode, however, exhibited an average calcium response slope of 30.1 mV, but only 8.9 mV for barium. This gives a slope ratio of 3.4:1, far different from the Nernstian value of 1:1. Thus it can be seen that the degree to which the activity dependence is decreased on using measured, rather than theoretical slope ratios, depends upon the degree to which the observed slope ratios deviate from the Nernstian ones.

It is equally clear from the results shown in Table 14 that the use of measured slope ratios rather than Nernstian ratios does not significantly affect the activity dependence of selectivity coefficients obtained using the mixed solution method with the graphical cross-point approach. The selectivity parameter $k^{XP}_{Ca,Ba}$, although different in magnitude, exhibits an activity dependence similar to that of the selectivity parameter $k^{XPR}_{Ca,Ba}$. In fact, for about half of

the data sets, the parameter $k^{XP}_{Ca,Ba}$ is slightly less activity dependent than is $k^{XPR}_{Ca,Ba}$. A possible explanation centers on the fact that the cross-point is determined by drawing the two best lines through the data points, and thus the cross-point in effect is obtained using measured rather than theoretical slopes. There is, then, in effect a slope correction inherent in the graphical approach. When Eqn. 42 is used to correct the values of $k^{XP}_{Ca,Ba}$ for the non-Nernstian slope ratio, the values of $k^{XPR}_{Ca,Ba}$ obtained have in effect been over-corrected. It is important to note, however, that the activity dependence of the values of either $k^{XP}_{Ca,Ba}$ or $k^{XPR}_{Ca,Ba}$ obtained by the graphical method is much greater than that of the values of $k^{R}_{Ca,Ba}$ obtained by the separate solution method.

The mixed solution data can be used to check the validity of the assumption (made in the separate solution method) that the electrode responds in the same manner to a one-component solution as it does to a multi-component solution. If this were true, then the slope of the line obtained at the high activity end of a plot of mixed solution data should be identical to the calibration slope observed for the ion whose activity was varied to obtain the set of mixed solution data. A comparison of these slopes (Tables 16, 17 and 20) clearly shows that this is not the case. For electrodes G1 and G2 in almost every instance the average of the slopes observed in mixed solution is higher

than that observed in pure solution. In addition the slopes observed in mixed solution when the activity of barium (the interfering ion) was varied decrease considerably as the activity of the fixed-concentration calcium ion is increased, although there is little activity dependence when the barium ion is the fixed-concentration ion. For electrodes Q1 and Q2 the slopes in mixed solutions, with very few exceptions, also are higher than those observed in pure solutions; again there is very little activity dependence of the slope when the interfering ion (calcium in this case) is the fixed-concentration ion. Thus, it appears that the presence of a second ion, even at very low activity, always affects the response of the electrode, but the effect is more pronounced when the second ion (the one present at lower activity) is the ion to which the electrode preferentially responds.

While it is clear that the slopes observed in separate and in mixed solution differ, it can be inferred from the results in Tables 18, 21, and 23 that this change in slope does not seriously affect the potential observed. These tables show a comparison of potentials measured in two-component mixed solutions with those calculated according to Eqn. 49 using selectivity coefficients ($k^{R}_{A,B}$) measured by the separate solution method using measured slopes. It can be seen that the difference between the measured and calculated potentials for electrodes G1 and G2 is usually 2 mV

or less. While this is a rather large difference on an absolute scale, especially when one considers that an error of only 0.1 mV in potential represents a 4% error in activity, it must be remembered that the potentials observed for G1 and G2 often varied by as much as 4 mV from day to day, and in addition that there was a problem with non-linearity which could not be totally overcome by restricting the activity range over which measurements were made. In view of these difficulties, then, a difference of only 2 mV between measured and calculated potentials is not excessive. The differences for electrodes Q1 and Q2 and for the Corning electrode are somewhat higher, averaging about 4 mV, but again this is within the reproducibility of the measurements.

Finally, while it can be seen that the selectivity coefficients measured using the separate solution method with measured slopes do an acceptable job of describing the behavior of the electrode in mixed solutions, it is clear from the results shown in Table 15 that a better fit can be obtained by using the curve-fitting approach. For electrode G1, for example, the average difference between measured and calculated potentials is about 0.5 mV. However, it must be remembered that the curve-fitting program obtains this low difference by varying the values of E^{o}, S and K to obtain the best fit for a particular set of points--if a different set of points is used a good fit can also be obtained, but

the values of E^{o}, S and K needed to obtain it may well be different from those which gave the best fit for the first set of points. This can be seen in the results shown in Table 15. The values of K calculated for electrodes G1 and G2 on days 1-3, when the calcium ion concentration was kept constant, have a relative standard deviation of 14% and 16% respectively. On days 4-6, when the barium concentration was kept constant, the relative standard deviations are 15% and 21% respectively. Thus, while it is possible to obtain a good fit for a particular set of data using the curve-fitting approach, the values of E^{o}, S and K thus obtained will not give a good fit when used with a different set of data.

CHAPTER 8
CONCLUSIONS

On the basis of this work several conclusions can be made:

1. The least dependence of the selectivity parameter on activity is obtained when the separate solution method is used, with measured rather than Nernstian slope ratios. The selectivity parameter thus obtained does a reasonable job of describing the electrode response in mixed solution. This method has the additional advantage of providing a check on the linearity of the response of the electrode.

2. The mixed solution/graphical cross-point method yields selectivity coefficients which are highly activity dependent. In addition, this method is not widely applicable, since it is not always possible to obtain two linear portions.

3. The mixed solution curve-fitting method can do an excellent job of fitting a particular set of data, but the values of the selectivity parameter obtained vary considerably.

4. Electrode response does appear to differ in mixed solutions as opposed to pure solutions. However, the difference does not appear to be significant when compared to the reproducibility of the measured potentials.

CHAPTER 9
SUGGESTIONS FOR FURTHER WORK

In this work a comparison has been made of several methods for the quantitative determination of electrode selectivity, with regard to the activity dependence and validity of the selectivity parameters obtained. However, no attempt has been made to compare the selectivity parameters measured to those which can in principle be calculated from the Eisenman, Buck and Morf theories regarding electrode response. The reason for this is simple--the parameters (such as ionic mobilities, dielectric constants and partitioning coefficients within the membrane) which appear in the theoretical equations often have not been measured, and in fact are in some instances not measurable using currently available techniques.

Buck and co-workers (29,60) have used AC impedance measurements to measure several properties of an Aliquat nitrate-PVC membrane, including the dielectric constant, ionic mobilities, equivalent conductances and ion-pairing constants. In addition, they have used the slope of the response of an electrode incorporating the membrane to determine the average site concentration in the membrane (28). It is suggested that an attempt be made to use these

methods to measure the properties of the membranes used in this work.

A second facet of this work which bears further investigation is the problem of non-Nernstian response slopes. While several authors have reported non-Nernstian behavior (40-42,61) little work has been done to identify the causes. Buck and co-workers have suggested that non-Nernstian slopes are the result of Donnan Exclusion failure and have shown, again with the Aliquat nitrate electrode, that as many as three regions of linear response, but with differing slopes, may be observed. The slopes measured for the Aliquat nitrate electrode have been compared to those predicted by the Teorell-Meyer-Sievers model when Donnan Exclusion fails, and excellent agreement has been found. It is suggested that the Teorell-Meyer-Sievers model be used to calculate theoretical slopes for the electrodes used in this work, under Donnan Exclusion failure, and that they be compared to the measured slopes. This will involve modifying the equations used in the model for the particular characteristics of these electrodes (e.g., mobile site neutral carrier with stong association), and measuring the parameters, such as ionic mobilities within the membrane, which determine the slope. Should good agreement be found between the theoretical and the measured slopes, it will serve as further proof that non-Nernstian behavior is a result of the failure of Donnan Exclusion.

Finally, it has been noted previously that the interpretation of the results of this experiment is somewhat uncertain, as a result of the rather poor reproducibility of the measured potentials. It would therefore be desirable to repeat these measurements using an electrode which is more reproducible, if such an electrode can be found.

In conclusion, then, future work should center on three aspects: confirmation of the conclusions made in this work regarding the best method for the determination of selectivity coefficients, investigation of Donnan Exclusion failure as a possible cause for non-Nernstian behavior and measurement of membrane properties (such as dielectric constants and ionic mobilities) so that theoretical values can be calculated for comparison to measured selectivity coefficients.

APPENDIX A

MIXED SOLUTION DATA FOR ELECTRODES G1 and G2

		ELECTRODE G1			ELECTRODE G2		
Ca Activity	Ba Activity	EMF-1	EMF-2	EMF-3	EMF-1	EMF-2	EMF-3
2.40×10^{-4}M	8.79×10^{-6}M	65.0mV	67.4mV	64.6mV	54.5mV	56.9mV	57.3mV
2.35×10^{-4}	9.32×10^{-5}	65.0	67.7	64.9	55.1	57.3	57.4
2.30×10^{-4}	1.75×10^{-4}	65.1	67.8	65.0	55.4	57.5	57.6
2.27×10^{-4}	2.54×10^{-4}	65.4	67.8	65.2	55.2	57.8	58.0
2.24×10^{-4}	3.30×10^{-4}	64.9	68.0	65.4	55.6	57.7	58.2
2.13×10^{-4}	5.99×10^{-4}	65.7	68.7	65.9	56.8	58.9	59.3
2.01×10^{-4}	9.69×10^{-4}	67.0	69.9	67.0	58.7	60.2	60.4
1.90×10^{-4}	1.41×10^{-3}	67.9	70.9	67.9	59.9	61.7	61.8
1.81×10^{-4}	1.83×10^{-3}	69.1	71.9	68.9	61.5	62.9	62.8
1.73×10^{-4}	2.20×10^{-3}	69.9	72.7	69.5	62.3	64.0	63.8
1.64×10^{-4}	2.73×10^{-3}	70.7	73.7	70.5	64.0	65.2	64.9
1.54×10^{-4}	3.57×10^{-3}	71.2	75.3	71.8	64.2	67.2	66.9
1.46×10^{-4}	4.33×10^{-3}	72.5	76.6	72.9	66.0	68.5	68.2
1.39×10^{-4}	5.04×10^{-3}	73.9	77.5	74.6	67.7	69.9	69.5
1.30×10^{-4}	6.36×10^{-3}	75.8	79.2	76.1	69.9	71.8	71.4
1.18×10^{-4}	8.05×10^{-3}	77.7	81.2	77.9	72.1	74.3	74.0
1.05×10^{-4}	1.04×10^{-2}	79.6	83.8	80.3	74.5	77.4	76.9
9.61×10^{-5}	1.25×10^{-2}	82.2	85.7	82.1	77.7	79.9	79.4
8.89×10^{-5}	1.43×10^{-2}	84.4	87.4	83.8	79.8	81.9	81.2
8.34×10^{-5}	1.60×10^{-2}	86.3	88.8	85.1	81.9	83.8	83.1

Ca Activity	Ba Activity	ELECTRODE G1			ELECTRODE G2		
		EMF-1	EMF-2	EMF-3	EMF-1	EMF-2	EMF-3
3.85×10^{-4}M	8.46×10^{-6}M	69.7mV	73.3mV	69.3mV	60.0mV	62.5mV	62.4mV
3.80×10^{-4}	9.04×10^{-5}	69.6	73.4	69.6	60.3	63.0	62.7
3.75×10^{-4}	1.70×10^{-4}	69.6	73.4	69.6	60.5	63.1	62.8
3.70×10^{-4}	2.47×10^{-4}	69.7	73.4	69.8	60.8	63.4	63.1
3.64×10^{-4}	3.22×10^{-4}	69.8	73.4	69.8	60.8	63.3	63.2
3.48×10^{-4}	5.86×10^{-4}	70.4	73.8	70.0	61.6	64.1	63.9
3.32×10^{-4}	9.53×10^{-4}	71.0	74.4	70.6	62.3	64.7	64.4
3.14×10^{-4}	1.40×10^{-3}	71.8	75.0	71.3	63.5	65.7	65.4
3.00×10^{-4}	1.81×10^{-3}	72.7	75.6	71.9	64.4	66.4	66.0
2.88×10^{-4}	2.19×10^{-3}	73.4	76.2	72.4	65.4	67.3	66.9
2.72×10^{-4}	2.72×10^{-3}	74.3	76.9	73.1	66.3	68.1	67.7
2.55×10^{-4}	3.55×10^{-3}	75.7	78.0	74.1	68.3	69.7	69.2
2.42×10^{-4}	4.31×10^{-3}	77.0	78.9	75.0	69.8	70.7	70.3
2.31×10^{-4}	5.01×10^{-3}	78.1	79.7	75.7	71.1	71.9	71.4
2.14×10^{-4}	6.29×10^{-3}	80.2	81.0	77.1	72.9	73.6	73.1
1.96×10^{-4}	7.98×10^{-2}	82.1	82.8	78.7	75.5	76.0	75.5
1.74×10^{-4}	1.04×10^{-2}	84.7	85.0	80.9	78.2	78.7	78.1
1.58×10^{-4}	1.26×10^{-2}	87.3	86.9	82.5	80.7	81.1	80.4
1.48×10^{-4}	1.45×10^{-2}	88.8	88.4	84.1	84.4	83.0	82.2
1.39×10^{-4}	1.62×10^{-2}	90.3	89.8	85.3	84.6	84.8	83.9

Ca Activity	Ba Activity	ELECTRODE G1 EMF-1	EMF-2	EMF-3	ELECTRODE G2 EMF-1	EMF-2	EMF-3
5.26×10^{-4}M	8.24×10^{-6}M	74.6mV	76.5mV	72.4mV	64.5mV	65.7mV	66.5mV
5.18×10^{-4}	8.83×10^{-5}	75.1	76.0	72.3	64.7	66.2	66.8
5.13×10^{-4}	1.66×10^{-4}	74.6	76.2	72.2	64.7	66.2	66.8
5.05×10^{-4}	2.42×10^{-4}	74.8	76.4	72.0	64.9	66.6	67.0
4.99×10^{-4}	3.16×10^{-4}	74.7	76.5	72.2	64.9	66.6	67.0
4.80×10^{-4}	5.76×10^{-4}	74.9	76.7	72.3	65.4	67.0	67.6
4.59×10^{-4}	9.40×10^{-4}	75.4	76.9	72.6	65.8	67.5	67.8
4.33×10^{-4}	1.38×10^{-3}	75.6	77.4	73.0	66.7	68.3	68.7
4.14×10^{-4}	1.80×10^{-3}	76.2	77.9	73.4	67.4	68.7	68.9
3.88×10^{-4}	2.18×10^{-3}	76.7	78.1	73.5	67.9	69.3	69.6
3.78×10^{-4}	2.70×10^{-3}	77.4	78.7	74.1	68.7	70.0	70.3
3.56×10^{-4}	3.54×10^{-3}	78.5	79.8	74.9	70.2	71.4	71.6
3.37×10^{-4}	4.30×10^{-3}	79.4	80.6	75.7	71.2	72.4	72.5
3.21×10^{-4}	5.00×10^{-3}	80.0	81.1	76.2	72.2	73.3	73.5
2.97×10^{-4}	6.25×10^{-3}	81.4	82.3	77.2	73.8	74.9	74.7
2.73×10^{-4}	7.98×10^{-3}	83.1	83.8	78.5	76.1	76.9	76.7
2.43×10^{-4}	1.04×10^{-2}	85.4	85.7	80.3	79.8	79.5	79.1
2.24×10^{-4}	1.25×10^{-2}	87.7	87.4	81.9	81.8	81.7	81.4
2.08×10^{-4}	1.45×10^{-2}	89.2	88.9	83.3	88.8	83.4	83.1
1.96×10^{-4}	1.63×10^{-2}	92.6	90.0	84.4	91.3	84.9	84.8

Ca Activity	Ba Activity	ELECTRODE G1 EMF-1	EMF-2	EMF-3	ELECTRODE G2 EMF-1	EMF-2	EMF-3
1.89×10^{-3}M	6.88×10^{-6}M	89.8mV	90.3mV	85.1mV	80.1mV	80.5mV	80.7mV
1.88×10^{-3}	7.42×10^{-5}	89.8	90.4	85.0	80.1	80.7	80.9
1.86×10^{-3}	1.40×10^{-4}	89.8	90.3	84.9	80.2	80.7	80.9
1.85×10^{-3}	2.06×10^{-4}	89.8	90.3	84.9	80.2	80.8	81.0
1.84×10^{-3}	2.71×10^{-4}	89.9	90.2	84.9	80.3	80.7	81.0
1.80×10^{-3}	5.02×10^{-4}	90.0	90.2	84.7	80.3	80.7	81.0
1.75×10^{-3}	8.32×10^{-4}	90.0	90.1	84.7	80.4	80.7	80.9
1.68×10^{-3}	1.25×10^{-3}	89.7	90.0	84.3	80.3	80.7	81.0
1.63×10^{-3}	1.63×10^{-3}	89.8	90.0	84.4	80.3	80.7	81.0
1.58×10^{-3}	1.99×10^{-3}	89.8	89.9	84.2	80.5	80.8	81.1
1.51×10^{-3}	2.50×10^{-3}	89.7	89.7	84.0	80.4	80.6	80.9
1.44×10^{-3}	3.32×10^{-3}	89.9	89.8	84.1	80.8	81.0	81.6
1.37×10^{-3}	4.05×10^{-3}	90.2	90.1	84.3	81.2	81.4	81.9
1.32×10^{-3}	4.75×10^{-3}	90.3	90.1	84.3	81.6	81.8	82.0
1.23×10^{-3}	6.01×10^{-3}	91.0	90.6	84.6	82.3	82.3	82.5
1.14×10^{-3}	7.71×10^{-3}	91.6	91.1	85.1	83.6	83.3	83.4
1.02×10^{-3}	1.01×10^{-2}	92.4	91.9	85.9	84.5	84.6	84.6
9.36×10^{-2}	1.21×10^{-2}	93.2	92.6	86.7	86.0	85.9	85.9
8.71×10^{-2}	1.40×10^{-2}	94.2	93.6	87.5	87.3	87.0	87.0
8.19×10^{-2}	1.56×10^{-2}	95.0	94.4	88.4	88.4	88.3	88.5

Ca Activity	Ba Activity	ELECTRODE G1 EMF-2	ELECTRODE G1 EMF-3	ELECTRODE G2 EMF-2	ELECTRODE G2 EMF-3
2.88×10^{-3}M	6.27×10^{-6}M	95.4mV	92.4mV	85.5mV	86.7mV
2.87×10^{-3}	6.77×10^{-5}	95.6	92.8	85.7	86.8
2.86×10^{-3}	1.29×10^{-4}	95.4	92.7	85.7	86.6
2.84×10^{-3}	1.89×10^{-4}	95.5	93.0	85.8	86.7
2.83×10^{-3}	2.48×10^{-4}	95.5	92.9	85.9	86.6
2.78×10^{-3}	4.65×10^{-4}	95.6	93.1	86.0	86.7
2.70×10^{-3}	7.72×10^{-4}	95.5	93.0	85.8	86.6
2.62×10^{-3}	1.16×10^{-3}	95.3	93.1	85.8	86.6
2.55×10^{-3}	1.53×10^{-3}	95.3	93.0	85.8	86.4
2.48×10^{-3}	1.87×10^{-3}	95.2	93.1	85.8	86.5
2.38×10^{-3}	2.37×10^{-3}	94.9	93.0	85.4	86.3
2.29×10^{-3}	3.16×10^{-3}	94.9	93.0	85.6	86.4
2.20×10^{-3}	3.90×10^{-3}	94.8	93.1	85.6	86.5
2.13×10^{-3}	4.59×10^{-3}	94.8	93.2	85.8	86.6
2.00×10^{-3}	5.86×10^{-3}	95.0	93.4	86.1	86.9
1.84×10^{-3}	7.54×10^{-3}	95.0	93.7	86.5	87.3
1.67×10^{-3}	9.93×10^{-2}	95.5	94.4	87.4	88.2
1.54×10^{-3}	1.21×10^{-2}	95.6	95.0	88.2	89.3
1.43×10^{-3}	1.40×10^{-2}	96.3	95.8	89.2	90.1
1.35×10^{-3}	1.56×10^{-2}	96.7	96.4	90.0	91.0

Ba Activity	Ca Activity	ELECTRODE G1 EMF-4	EMF-5	EMF-6	ELECTRODE G2 EMF-4	EMF-5	EMF-6
1.88×10^{-3}M	6.93×10^{-6}M	68.6mV	69.2mV	55.3mV	58.0mV	57.1mV	52.4mV
1.87×10^{-3}	7.47×10^{-5}	71.7	71.1	57.9	61.2	60.0	55.3
1.86×10^{-3}	1.41×10^{-4}	73.6	73.6	59.9	63.2	62.3	57.3
1.84×10^{-3}	2.08×10^{-4}	75.6	75.5	61.7	64.9	64.0	59.3
1.83×10^{-3}	2.73×10^{-4}	76.9	77.3	63.1	66.5	65.7	60.6
1.79×10^{-3}	5.07×10^{-4}	81.5	82.2	67.8	71.1	70.0	65.4
1.74×10^{-3}	8.40×10^{-4}	85.9	86.7	72.3	75.2	74.5	69.7
1.67×10^{-3}	1.26×10^{-3}	89.7	90.5	76.1	79.2	78.3	73.8
1.61×10^{-3}	1.65×10^{-3}	92.5	93.3	78.8	81.9	81.1	76.4
1.56×10^{-3}	2.02×10^{-3}	94.6	95.4	80.9	84.1	83.2	78.6
1.49×10^{-3}	2.54×10^{-3}	97.1	98.0	83.4	86.5	85.6	80.9
1.41×10^{-3}	3.38×10^{-3}	00.1	01.0	86.5	89.8	88.7	84.3
1.35×10^{-3}	4.15×10^{-3}	02.3	98.6	88.9	91.9	90.8	86.5
1.29×10^{-3}	4.87×10^{-3}	04.1	00.2	90.8	93.8	92.7	88.6
1.21×10^{-3}	6.17×10^{-3}	06.9	03.1	93.6	96.5	95.4	91.3
1.09×10^{-3}	7.94×10^{-3}	10.0	06.3	96.9	99.7	98.7	94.8
9.79×10^{-4}	1.05×10^{-2}	13.8	09.7	00.7	103.3	01.8	98.4
8.98×10^{-4}	1.29×10^{-2}	16.3	12.2	03.3	105.9	04.7	01.3
8.33×10^{-4}	1.49×10^{-2}	18.3	14.1	05.4	107.9	06.5	03.2
7.82×10^{-4}	1.68×10^{-2}	19.9	15.7	07.1	109.7	08.4	05.0

Ba Activity	Ca Activity	ELECTRODE G1 EMF-4	EMF-5	EMF-6	ELECTRODE G2 EMF-4	EMF-5	EMF-6
2.85×10^{-3}M	6.34×10^{-6}M	72.0mV	67.9mV	58.2mV	62.3mV	60.9mV	56.5mV
2.84×10^{-3}	6.82×10^{-5}	74.1	70.1	60.5	64.4	63.2	58.7
2.82×10^{-3}	1.30×10^{-4}	75.7	71.8	61.9	65.9	64.7	60.0
2.81×10^{-3}	1.90×10^{-4}	77.0	73.2	63.3	67.2	66.1	61.4
2.80×10^{-3}	2.51×10^{-4}	78.1	74.3	64.4	68.3	67.2	62.5
2.75×10^{-3}	4.69×10^{-4}	82.1	78.3	68.5	71.9	71.0	66.5
2.68×10^{-3}	7.80×10^{-4}	5.98	82.2	72.6	75.8	74.7	70.4
2.59×10^{-3}	1.17×10^{-3}	89.5	85.8	76.3	79.3	78.3	74.1
2.53×10^{-3}	1.55×10^{-3}	92.0	88.4	79.0	81.7	80.8	76.7
2.44×10^{-3}	1.90×10^{-3}	94.0	90.3	81.0	83.8	82.8	78.9
2.35×10^{-3}	2.41×10^{-3}	96.4	92.7	83.7	86.2	85.3	81.4
2.24×10^{-3}	3.22×10^{-3}	99.4	95.7	86.8	89.2	88.4	84.7
2.15×10^{-3}	3.96×10^{-3}	01.5	97.9	89.1	91.4	90.5	86.9
2.07×10^{-3}	4.68×10^{-3}	03.3	99.8	90.9	93.3	92.5	88.9
1.95×10^{-3}	5.99×10^{-3}	06.1	02.5	93.9	96.0	95.1	91.9
1.79×10^{-3}	7.78×10^{-3}	09.3	05.7	97.2	99.2	98.4	95.3
1.61×10^{-3}	1.04×10^{-2}	12.8	09.2	00.8	102.6	01.7	98.9
1.48×10^{-3}	1.26×10^{-2}	15.4	11.8	03.5	105.4	04.6	01.8
1.37×10^{-3}	1.46×10^{-2}	17.4	13.8	05.5	107.4	06.5	03.9
1.29×10^{-3}	1.65×10^{-2}	19.0	15.5	07.1	109.0	08.3	05.8

Ba Activity	Ca Activity	ELECTRODE G1 EMF-5	ELECTRODE G1 EMF-6	ELECTRODE G2 EMF-5	ELECTRODE G2 EMF-6
4.90×10^{-3}M	5.46×10^{-6}M	81.7mV	67.0mV	67.5mV	63.0mV
4.88×10^{-3}	5.90×10^{-5}	83.3	67.2	68.7	64.5
4.86×10^{-3}	1.12×10^{-4}	85.8	68.4	69.4	65.5
4.85×10^{-3}	1.65×10^{-4}	85.9	69.2	70.3	66.4
4.82×10^{-3}	2.17×10^{-4}	87.0	70.2	71.2	67.4
4.75×10^{-3}	4.08×10^{-4}	89.7	73.0	73.7	70.2
4.67×10^{-3}	6.87×10^{-4}	93.0	76.3	76.6	76.4
4.56×10^{-3}	1.04×10^{-3}	96.0	79.3	79.4	76.4
4.46×10^{-3}	1.38×10^{-3}	98.6	82.0	81.8	78.9
4.35×10^{-3}	1.71×10^{-3}	00.4	83.8	83.6	80.8
4.22×10^{-3}	2.17×10^{-3}	02.7	86.2	85.8	83.2
4.08×10^{-3}	2.94×10^{-3}	04.3	89.5	88.7	86.4
3.96×10^{-3}	3.65×10^{-3}	06.8	92.0	91.0	88.7
3.84×10^{-3}	4.34×10^{-3}	09.9	93.8	92.7	90.8
3.64×10^{-3}	5.60×10^{-3}	12.8	96.7	95.6	93.5
3.39×10^{-3}	7.40×10^{-3}	15.7	99.9	98.9	97.2
3.06×10^{-3}	9.96×10^{-2}	19.6	04.0	02.5	01.0
2.84×10^{-3}	1.23×10^{-2}	22.0	07.0	05.3	04.1
2.65×10^{-3}	1.43×10^{-2}	24.2	09.2	07.4	06.3
2.50×10^{-3}	1.62×10^{-2}	25.7	11.2	09.2	08.2

APPENDIX B

MIXED SOLUTION DATA FOR ELECTRODES Q1 and Q2

Activity Na	Activity Ca	EMF-1	EMF-2	EMF-3	EMF-4	EMF-5	EMF-6	EMF-7	EMF-8	EMF-9	EMF-10	EMF-11	EMF-12
8.35×10^{-6}M	2.87×10^{-3}M	-36.9mV	-36.6mV	-35.0mV	-35.0mV	-34.7mV	-40.6mV	-36.5mV	-38.3mV	-41.1mV	-42.0mV	-41.4mV	-43.4mV
1.67×10^{-4}	2.87×10^{-3}	-34.1	-34.0	-32.4	-32.4	-32.0	-37.6	-34.2	-35.9	-36.6	-39.4	-36.9	-40.9
3.33×10^{-4}	2.85×10^{-3}	-28.6	-29.7	-28.0	-27.9	-28.3	-32.9	-30.4	-31.8	-34.3	-35.0	-34.8	-36.2
5.80×10^{-4}	2.83×10^{-3}	-22.8	-23.7	-22.3	-22.1	-22.7	-26.5	-24.9	-26.1	-28.1	-28.6	-28.9	-30.0
9.06×10^{-4}	2.81×10^{-3}	-16.6	-17.5	-16.4	-16.0	-17.4	-19.8	-18.8	-19.8	-21.6	-22.4	-22.5	-23.5
1.23×10^{-3}	2.79×10^{-3}	-11.5	-12.5	-11.4	-10.9	-12.5	-14.7	-14.3	-14.9	-16.4	-17.5	-17.4	-18.1
1.55×10^{-3}	2.76×10^{-3}	- 7.8	- 8.7	- 7.5	- 6.9	- 8.5	-10.4	-10.5	-10.9	-12.0	-12.5	-12.5	-13.7
2.03×10^{-3}	2.73×10^{-3}	- 2.2	- 3.6	- 2.2	- 1.8	- 3.8	- 5.1	- 5.7	- 5.7	- 7.0	- 7.4	- 7.5	- 8.6
2.86×10^{-3}	2.69×10^{-3}	4.1	2.6	4.1	5.3	1.8	1.9	1.2	1.0	- 0.2	- 0.9	- 1.2	- 1.6
4.52×10^{-3}	2.63×10^{-3}	14.1	12.2	13.7	14.7	10.5	11.1	10.6	10.4	9.4	8.7	8.5	8.7
6.16×10^{-3}	2.57×10^{-3}	21.9	18.6	20.3	21.3	17.3	18.3	17.3	17.1	16.5	15.0	15.5	15.1
8.57×10^{-3}	2.49×10^{-3}	29.0	26.2	27.7	28.7	24.1	25.6	24.5	24.7	24.0	22.4	23.0	22.8
1.25×10^{-2}	2.38×10^{-3}	37.4	34.5	35.8	37.0	32.3	33.5	33.1	32.9	32.0	31.5	31.8	31.5
2.00×10^{-2}	2.20×10^{-3}	48.4	45.5	47.1	47.9	42.1	44.4	44.1	44.0	43.2	42.5	42.9	42.4
Electrode Q2													
8.35×10^{-5}M	2.87×10^{-3}M	-30.0mV	-29.4mV	-23.0mV	-19.6mV	-24.8mV	-26.4mV	-23.5mV	-23.1mV	-25.0mV	-26.9mV	-28.5mV	
1.67×10^{-4}	2.87×10^{-3}	-27.7	-27.9	-21.4	-15.9	-23.2	-23.8	-21.9	-20.8	-23.2	-24.9	-25.9	
3.33×10^{-4}	2.85×10^{-3}	-22.7	-23.1	-16.8	-11.3	-18.8	-19.2	-16.2	-16.7	-19.2	-20.9	-22.6	
5.80×10^{-4}	2.83×10^{-3}	-17.6	-17.7	-12.0	- 5.9	-13.4	-13.3	-13.2	-11.5	-14.0	-15.8	-16.0	
9.06×10^{-4}	2.81×10^{-3}	-11.4	-11.6	- 5.9	0.0	- 7.5	- 7.3	- 8.0	- 6.1	- 8.3	-10.2	-11.7	
1.23×10^{-3}	2.79×10^{-3}	- 6.6	- 7.2	- 1.3	4.6	- 2.6	- 2.4	- 4.0	- 1.9	- 3.7	- 5.8	- 6.7	
1.55×10^{-3}	2.76×10^{-3}	- 2.5	- 3.2	2.7	8.3	1.2	1.5	- 0.4	1.9	0.13	- 1.9	- 3.6	
2.03×10^{-3}	2.73×10^{-3}	2.4	1.2	7.3	13.2	5.9	6.3	4.6	6.4	5.2	2.9	1.7	
2.86×10^{-3}	2.69×10^{-3}	9.0	7.5	13.6	19.5	12.2	12.9	10.8	12.9	11.5	9.4	7.2	
4.52×10^{-3}	2.63×10^{-3}	18.5	16.2	22.7	27.6	21.2	22.4	19.8	21.8	20.5	17.7	17.7	
6.16×10^{-3}	2.57×10^{-3}	25.3	22.9	29.4	34.0	27.6	29.1	26.3	28.3	27.3	24.2	23.3	
8.57×10^{-3}	2.49×10^{-3}	32.3	30.0	36.1	41.7	35.0	36.1	33.2	35.5	34.6	31.0	30.4	
1.25×10^{-2}	2.38×10^{-3}	41.1	38.6	44.7	49.2	43.4	44.2	41.7	43.4	43.0	39.8	38.7	
2.00×10^{-2}	2.20×10^{-3}	51.9	47.5	57.1	59.8	53.4	52.7	52.1	54.0	54.6	50.6	46.6	

Activity Na	Activity Ca	EMF-1	EMF-2	EMF-3	EMF-4	EMF-5	EMF-6
8.18×10^{-5}M	3.75×10^{-3}M	-35.0mV	-36.9mV	-33.1mV	-34.6mV	-28.0mV	-40.4mV
1.63×10^{-4}	3.75×10^{-3}	-32.6	-34.3	-30.9	-32.3	-26.4	-37.7
3.26×10^{-4}	3.73×10^{-3}	-28.2	-30.3	-27.4	-28.8	-24.6	-32.7
5.69×10^{-4}	3.71×10^{-3}	-22.3	-24.0	-21.6	-23.1	-19.5	-27.0
8.89×10^{-4}	3.68×10^{-3}	-16.5	-17.5	-16.1	-17.0	-14.6	-20.5
1.21×10^{-3}	3.65×10^{-3}	-11.2	-12.1	-10.7	-12.1	-10.0	-15.3
1.52×10^{-3}	3.63×10^{-3}	- 6.8	- 8.2	- 6.9	- 8.6	- 7.0	-10.9
1.99×10^{-3}	3.59×10^{-3}	- 1.7	- 2.9	- 1.9	- 3.3	- 2.2	- 5.3
2.81×10^{-3}	3.55×10^{-3}	4.9	4.0	4.7	3.4	3.6	1.0
4.45×10^{-3}	3.48×10^{-3}	14.4	13.5	14.3	13.1	12.4	10.6
6.06×10^{-3}	3.41×10^{-3}	21.8	19.8	20.8	20.4	18.5	17.0
8.44×10^{-3}	3.32×10^{-3}	29.2	27.3	28.3	27.6	25.5	24.6
1.23×10^{-2}	3.18×10^{-3}	38.0	35.6	37.1	36.2	34.4	32.5
1.98×10^{-2}	2.96×10^{-3}	48.5	46.6	48.3	46.9	45.1	43.8
Electrode Q2							
8.18×10^{-5}M	3.75×10^{-3}M	-27.6mV	-28.9mV	-23.8mV	-24.5mV	-19.2mV	-27.5mV
1.63×10^{-4}	3.75×10^{-3}	-25.9	-26.9	-21.9	-22.5	-18.8	-24.9
3.26×10^{-4}	3.73×10^{-3}	-21.4	-22.4	-17.7	-18.1	-14.9	-20.6
5.69×10^{-4}	3.71×10^{-3}	-16.1	-16.9	-12.3	-12.6	-10.8	-15.0
8.89×10^{-4}	3.68×10^{-3}	-10.5	-10.9	- 6.7	- 6.9	- 5.4	- 9.3
1.21×10^{-3}	3.65×10^{-3}	- 5.8	- 6.2	- 1.6	- 2.0	- 1.8	- 4.0
1.52×10^{-3}	3.63×10^{-3}	- 1.8	- 2.3	2.2	2.0	2.2	- 0.1
1.99×10^{-3}	3.59×10^{-3}	3.3	2.5	6.7	13.5	6.4	4.4
2.81×10^{-3}	3.55×10^{-3}	9.5	9.2	13.3	19.9	12.7	10.8
4.45×10^{-3}	3.48×10^{-3}	18.3	18.1	22.0	26.6	21.2	20.1
6.06×10^{-3}	3.41×10^{-3}	25.2	24.8	28.6	32.9	27.6	26.6
8.44×10^{-3}	3.32×10^{-3}	32.2	32.1	35.2	38.6	34.4	32.9
1.23×10^{-2}	3.18×10^{-3}	41.0	40.6	43.6	46.5	42.8	41.9
1.98×10^{-2}	2.96×10^{-3}	49.7	51.1	53.7	56.3	53.5	52.0

Electrode Q1

Activity Na	Activity Ca	EMF-1	EMF-2	EMF-3	EMF-4	EMF-5	EMF-6	EMF-7	EMF-8	EMF-9	EMF-10	EMF-11	EMF-12
7.55×10^{-5}M	8.22×10^{-3}M	-20.8mV	-26.9mV	-23.2mV	-22.1mV	-23.5mV	-27.0mV	-27.9mV	-29.5mV	-31.1mV	-33.1mV	-33.4mV	-32.7mV
1.51×10^{-4}	8.21×10^{-3}	-19.5	-25.2	-21.6	-20.8	-21.9	-25.5	-26.5	-28.0	-29.6	-31.5	-31.6	-31.4
3.01×10^{-4}	8.19×10^{-3}	-17.1	-22.2	-18.3	-19.3	-19.5	-24.0	-24.0	-25.4	-26.7	-28.6	-28.9	-28.3
5.25×10^{-4}	8.15×10^{-3}	-13.5	-17.8	-14.7	-15.2	-15.6	-19.9	-20.2	-21.4	-22.8	-24.2	-24.6	-24.0
8.21×10^{-4}	8.11×10^{-3}	- 9.5	-13.4	-10.9	-11.3	-11.4	-15.8	-16.0	-17.0	-18.1	-19.6	-19.4	-19.2
1.12×10^{-3}	8.06×10^{-3}	- 5.9	- 9.0	- 7.2	- 7.4	- 7.6	-11.6	-12.1	-12.9	-13.8	-15.2	-15.1	-15.1
1.41×10^{-4}	8.02×10^{-3}	- 2.9	- 5.6	- 4.4	- 4.1	- 4.2	-10.0	- 8.9	- 9.6	-10.4	-11.6	-11.6	-11.3
1.84×10^{-3}	7.96×10^{-3}	- 1.1	- 1.1	- 0.1	0.1	0.0	5.3	- 4.6	- 5.3	- 6.0	- 6.9	- 6.8	- 6.9
2.61×10^{-3}	7.91×10^{-3}	7.1	4.7	4.8	6.0	5.5	0.8	1.2	0.0	0.4	- 0.8	- 0.6	- 0.4
4.13×10^{-3}	7.82×10^{-3}	15.5	13.7	13.5	14.6	14.1	10.4	10.0	8.9	9.2	8.3	8.5	8.9
5.64×10^{-3}	7.74×10^{-3}	21.7	20.0	19.0	20.8	20.3	17.0	16.3	14.5	16.1	14.8	14.9	15.7
7.87×10^{-3}	7.62×10^{-3}	28.7	27.2	26.5	27.9	27.5	24.1	23.5	22.1	23.3	22.2	22.4	23.0
1.16×10^{-2}	7.43×10^{-3}	36.9	34.8	34.4	35.9	35.7	32.2	32.2	30.0	31.9	30.3	31.0	31.5
1.87×10^{-2}	7.10×10^{-3}	47.4	45.8	45.6	46.7	46.4	43.1	43.0	40.9	42.5	41.6	42.1	42.4

Electrode Q2

7.55×10^{-5}M	8.22×10^{-3}M	-14.3mV	-18.9mV	-12.1mV	-15.3mV	-13.9mV	- 9.5mV	-15.1mV	-14.6mV	-14.1mV	-18.2mV	-19.2mV
1.51×10^{-4}	8.21×10^{-3}	-13.6	-17.7	-10.1	-14.6	-12.9	- 9.6	-14.2	-13.4	-12.9	-17.3	-18.4
3.01×10^{-4}	8.19×10^{-3}	-11.3	-14.6	- 7.5	-11.9	-10.3	- 7.0	-11.8	-10.6	-10.3	-14.5	-16.0
5.25×10^{-4}	8.15×10^{-3}	- 8.3	-11.2	- 5.4	- 8.3	- 6.5	- 5.0	- 8.6	- 7.1	- 7.1	-11.0	-11.1
8.21×10^{-4}	8.11×10^{-3}	- 4.5	- 6.6	- 1.4	- 4.2	- 2.3	- 0.9	- 4.8	- 2.9	- 2.9	- 6.6	- 7.7
1.12×10^{-3}	8.06×10^{-3}	- 0.9	- 2.7	- 1.8	- 0.4	- 1.5	- 0.6	- 1.5	- 0.1	0.3	- 3.5	- 3.9
1.41×10^{-4}	8.02×10^{-3}	2.1	0.5	5.0	2.7	4.5	2.5	1.6	3.0	- 3.5	- 0.2	- 1.4
1.84×10^{-3}	7.96×10^{-3}	5.9	4.9	8.3	6.6	8.6	5.6	5.6	6.7	6.9	4.2	2.3
2.61×10^{-3}	7.91×10^{-3}	11.2	10.7	13.9	12.3	14.1	11.6	10.9	12.4	12.4	9.9	7.8
4.13×10^{-3}	7.82×10^{-3}	18.8	19.4	19.9	20.8	22.5	20.0	19.0	19.7	20.0	17.8	17.1
5.64×10^{-3}	7.74×10^{-3}	24.8	24.4	26.0	27.0	28.4	26.5	25.0	25.8	26.4	24.1	22.8
7.87×10^{-3}	7.62×10^{-3}	31.4	30.4	31.9	33.8	35.2	32.9	31.4	32.0	32.9	30.9	31.3
1.16×10^{-2}	7.43×10^{-3}	39.5	38.8	40.2	41.9	43.4	41.1	39.6	40.0	41.2	39.3	38.7
1.87×10^{-2}	7.10×10^{-3}	49.7	49.3	50.1	52.4	54.0	52.0	50.2	50.1	52.0	49.8	48.1

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BIOGRAPHICAL SKETCH

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Ms. Dixon attended the Pensacola Junior College and the University of West Florida on a National Merit Scholarship. While at the University of West Florida she participated in a cooperative education program, working at The American Cyanamid plant in Milton, Florida, and the U.S. Environmental Protection Agency Laboratory in Gulf Breeze, Florida. She received the Associate of Arts degree from Pensacola Junior College with highest honors in August of 1974, and the Bachelor of Science degree in chemistry summa cum laude from The University of West Florida in June of 1976. In August of 1978 she received the Master of Arts degree in chemistry from Duke University.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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Graduate Research Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

James D. Winefordner
Graduate Research Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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August 1986

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